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(71)出願人　000005821
松下電器産業株式会社
大阪府門真市大字門真1006番地

(71)出願人　000005968
三菱化学株式会社
東京都千代田区丸の内二丁目５番２号

(72)発明者　北川　雅規
大阪府門真市大字門真1006番地　松下電器産業株式会社内

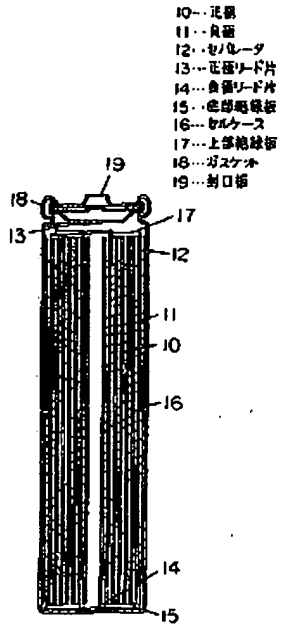
(72)発明者　越名　秀
大阪府門真市大字門真1006番地　松下電器産業株式会社内

(74)代理人　弁理士　石原　勝

最終頁に続く

(54)【発明の名称】　非水電解質二次電池

(57)【要約】
【課題】　非水電解液二次電池二次電池の高温での保存特性や低温での放電特性の向上を図る。
【解決手段】　所定の面間隔、スペクトル値、平均粒径、比表面積、タッピング密度、（１１０）／（００４）Ｘ線ピーク強度比を有する黒鉛核の表層を炭素質物で被覆した負極材を用いた非水電解液二次電池。



【特許請求の範囲】

【請求項１】 正極と負極とこれらの間に配されるセパレータを備え、前記負極は、充電および放電によりリチウムイオンがインターカレーションおよびディインターカレーションを可逆的に繰り返すことができる負極材料として、以下の特性を示す塊状の黒鉛粉末を核とし、その核の表面に炭素前駆体を被覆後、不活性ガス雰囲気下で７００～２８００℃の温度範囲で焼成し、炭素質物の表層を形成させた複層構造の炭素質粉末を用いた非水電解質二次電池。

（１）広角Ｘ線回折法による（００２）面の面間隔（ｄ００２）が３．３７Å未満でかつＣ軸方向の結晶子の大きさ（Ｌｃ）が少なくとも１０００Å以上

（２）アルゴンイオンレーザーラマンスペクトルにおける１５８０ｃｍ$^{-1}$のピーク強度に対する１３６０ｃｍ$^{-1}$のピーク強度比であるＲ値が０．３以下でかつ１５８０ｃｍ$^{-1}$ピークの半値幅が２４ｃｍ$^{-1}$以下

（３）平均粒径が１０～３０μｍでかつ一番薄い部分の厚さの平均値が少なくとも３μｍ以上平均粒径以下

（４）ＢＥＴ法による比表面積が３．５ｍ^2／ｇ以上１０．０ｍ^2／ｇ以下

（５）タッピング密度が０．５ｇ／ｃｃ以上１．０ｇ／ｃｃ以下

（６）広角Ｘ線回折法による（１１０）／（００４）のＸ線回折ピーク強度比が０．０１５以上

【請求項２】 核に用いる黒鉛の平均円形度が０．９４０以上である請求項１に記載の非水電解質二次電池。

【請求項３】 複層構造の炭素質粉末材料のタッピング密度が０．７ｇ／ｃｃ以上１．２ｇ／ｃｃ以下である請求項１又は２に記載の非水電解質二次電池。

【請求項４】 複層構造の炭素質粉末材料のＢＥＴ法による比表面積が１．０～５．０ｍ^2／ｇである請求項１～３のいずれかに記載の非水電解質二次電池。

【請求項５】 複層構造の炭素質粉末材料の平均粒径が１１～４０μｍであり、一番薄い部分の厚さの平均値が４μｍ以上平均粒径以下の請求項１～４のいずれかに記載の非水電解質二次電池。

【請求項６】 正極と負極とこれらの間に配されるセパレータを備え、前記正極はリチウム含有酸化物（化学式ＬｉｘＭＯ$_2$、ただし、ＭはＣｏ、Ｎｉ、Ｍｎ、Ｆｅから選ばれる１種以上の遷移金属、ｘ＝０以上１．２以下）を活物質とし、前記負極は、充電および放電によりリチウムイオンがインターカレーションおよびディインターカレーションを可逆的に繰り返すことができる負極材料として、以下の特性を示す塊状の黒鉛粉末を核とし、その核の表面に炭素前駆体を被覆後、不活性ガス雰囲気下で７００～２８００℃の温度範囲で焼成し、炭素質物の表層を形成させた複層構造の炭素質粉末を用いた非水電解質二次電池。

（１）広角Ｘ線回折法による（００２）面の面間隔（ｄ００２）が３．３７Å未満でかつＣ軸方向の結晶子の大きさ（Ｌｃ）が少なくとも１０００Å以上

（２）アルゴンイオンレーザーラマンスペクトルにおける１５８０ｃｍ$^{-1}$のピーク強度に対する１３６０ｃｍ$^{-1}$のピーク強度比であるＲ値が０．３以下でかつ１５８０ｃｍ$^{-1}$ピークの半値幅が２４ｃｍ$^{-1}$以下

（３）平均粒径が１０～３０μｍでかつ一番薄い部分の厚さの平均値が少なくとも３μｍ以上平均粒径以下

（４）ＢＥＴ法による比表面積が３．５ｍ^2／ｇ以上１０．０ｍ^2／ｇ以下

（５）タッピング密度が０．５ｇ／ｃｃ以上１．０ｇ／ｃｃ以下

（６）広角Ｘ線回折法による（１１０）／（００４）のＸ線回折ピーク強度比が０．０１５以上

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、非水電解質二次電池に係り、特にリチウムイオン二次電池の負極用炭素材に関する。

【０００２】

【従来の技術】従来、非水電解質二次電池としては、高電圧、高容量による高エネルギー密度化を志向して、負極活物質として金属リチウム、正極活物質として遷移金属の酸化物や硫化物やセレン化物等のカルコゲン化合物、例えば二酸化マンガンや二硫化モリブデンやセレン化チタンなど、非水電解質としてリチウム塩の有機溶媒溶液からなる有機電解液を用いた、いわゆるリチウム二次電池が検討されている。

【０００３】しかしながら、このリチウム二次電池は、正極活物質として比較的充放電特性が優れた層間化合物を選択することができるが、負極の金属リチウムの充放電特性は必ずしも優れていない。そのために、充放電を繰り返すサイクル寿命を長くすることが難しく、その上、内部短絡による発熱が起こる恐れがあり、安全性に問題があった。すなわち、負極活物質の金属リチウムは放電により有機電解液中にリチウムイオンとして溶出する。溶出したリチウムイオンは充電により、金属リチウムとして負極表面に析出するが、元のようにすべて平滑に析出せずに、樹枝状または苔状の活性な金属結晶として析出するものがある。活性な金属結晶は電解液中の有機溶媒を分解するとともに、金属結晶自体の表面は不動態被膜で覆われて不活性化し、放電に寄与し難くなる。その結果、充放電サイクルが進むにつれて負極容量が低下するので、セル作製時に、負極容量を正極のそれより著しく大きくする必要があった。また、活性な樹枝状金属リチウム結晶は、セパレータを貫通して正極と接触して、内部短絡する場合がある。内部短絡により、セルは発熱する恐れがある。

【０００４】そこで、負極材料として充電および放電により、インターカレーションおよびディインターカレー

ションを可逆的に繰り返すことができる炭素材を用いる．いわゆるリチウムイオン二次電池が提案され．活発に研究開発されて、すでに実用化段階を迎えている。このリチウムイオン二次電池は過充電しない限り．充放電時に．負極表面に活性な樹枝状金属リチウム結晶が析出しないので、安全性の向上が大いに期待できる。さらに．この電池は金属リチウムを負極活物質に用いるリチウム二次電池よりも高率充放電特性とサイクル寿命が著しく優れているので、近年この電池の需要は急速に伸張している。

【0005】4V級のリチウムイオン二次電池の正極活物質としては．放電状態に相当する$LiCoO_2$．$LiNiO_2$、$LiMnO_2$．$Li_1Mn_2O_4$などのリチウムと遷移金属の複合酸化物が採用または検討されている。電解質としては、リチウム二次電池と同様に有機電解液やポリマー固体電解質等の非水電解質が用いられる。

【0006】負極材料に黒鉛を用いた場合、リチウムイオンがインターカレーションされて生成する層間化合物のC_6Liを基準にした炭素1g当たりの容量の理論値は372mAhである。従って、種々の炭素材において．この比容量の理論値に近付き、かつ実用電池の負極としては、単位体積当たりの容量値．すなわち．容量密度（mAh／cc）が可及的に高くなるものを選ぶべきである。

【0007】各種炭素材のうち、俗にハードカーボンと称される難黒鉛化炭素において、前記した比容量理論値（372mAh／g）を越える材料が見出されて検討が進められている。しかし．難黒鉛化性の非晶質炭素の真比重は小さく．嵩張るので．負極の容量密度を大きくするのは実質的に困難である。その上．充電後の負極電位が金属リチウム電位に近似する程卑とはいえず．放電電位は平坦性も劣る等の課題が多い。

【0008】これに対して．結晶性が高い天然黒鉛および人造黒鉛粉末を負極に用いた場合．充電後の電位は金属リチウム電位に近似し．かつ放電電位の平坦性も優れており、実用電池として．充放電特性が向上するので、最近では黒鉛系粉末が負極材料の主流となりつつある。

【0009】そのなかにあって、リチウムイオン二次電池の負極用黒鉛粉末の平均粒径が大きければ、高率での充放電特性および低温における放電特性が劣る傾向がある。

【0010】そこで、粉末の平均粒径を小さくすれば、高率充放電特性および低温放電特性は向上するが．徒らに平均粒径を小さくし過ぎると、粉末の比表面積が大きくなり過ぎることによって．初充電により粉末中に挿入されたリチウムが第1サイクル以降の放電に寄与できない不可逆容量が大きくなる問題が生ずる。この現象は高エネルギー密度化志向に対して致命的な欠点であるとともに．100℃を越えるような高温下で電池を放置した場合．有機電解液中の溶媒を分解させて、自己放電するだけでなく、セル内圧を高めて漏液事故を起こす恐れがあり．電池の信頼性を低下させる原因となっていた。

【0011】以上のことから、負極用黒鉛粉末には適切な比表面積および平均粒径が重要になることは容易に理解される。そのような観点から提案された発明が例えば．特開平6-295725号公報において、BET法による比表面積が1～10m^2／gであり．平均粒径が10～30μmであり、かつ、粒径10μm以下の粉末の含有率および粒径30μm以上の粉末の含有率の少なくとも一方が10%以下である黒鉛粉末を使用することが開示されている。さらに．特開平7-134988号公報においては．石油ピッチを低温で熱処理して生成するメソカーボンマイクロビーズを黒鉛化し、広角X線回折法による（002）面の面間隔（d002）が3．36～3．40Åで、BET法による比表面積が0．7～5．0m^2／gである球状黒鉛粉末を使用することが開示されている。また、特開平5-307959号公報において比表面積が20m^2／g以下で該の炭素物質の1／2以下の比表面積を有する多相炭素物質を使用することが開示されている。

【0012】

【発明が解決しようとする課題】前述した発明は．リチウムイオン二次電池の高率充放電特性および低温時の放電特性の向上に極めて効果的であるだけでなく．宿命的ともいえる、サイクル初期に決定づけられる不可逆容量の低減に効果的であった。しかし、高温下での放置による保存性や信頼性に対して不十分であり、負極の比容量（mAh／g）および容量密度（mAh／cc）の点でも不満が残っていた。本発明は、リチウム二次電池のさらなる信頼性および高エネルギー密度化の改善をはかることをその目的とする。

【0013】

【課題を解決するための手段】前述したリチウムイオン二次電池における課題を解決するために、本発明は、

（1）広角X線回折法による（002）面の面間隔（d002）が3．37Å未満でかつC軸方向の結晶子の大きさ（Lc）が少なくとも1000Å以上

（2）アルゴンイオンレーザーラマンスペクトルにおける1580cm^{-1}のピーク強度に対する1360cm^{-1}のピーク強度比であるR値が0．3以下でかつ1580cm^{-1}ピークの半値幅が24cm^{-1}以下

（3）平均粒径が10～30μmでかつ一番薄い部分の厚みが少なくとも3μm以上平均粒径以下

（4）BET法による比表面積が3．5m^2／g以上10．0m^2／g以下

（5）タッピング密度が0．5g／cc以上1．0g／cc以下

（6）広角X線回折法による（110）／（004）のX線回折ピーク強度比が0．015以上の特性を示す塊

状の黒鉛粉末を核とし、その核の表面に炭素前駆体を被覆後．不活性ガス雰囲気下で７００～２８００℃の温度範囲で焼成し．炭素質物の表層を形成させた複層構造の炭素質粉末を負極材料として用いることにより．初期サイクルに認められる不可逆容量を可及的に小さくすると共に．高温下での放置における電池の保存性および信頼性を向上し、優れた高率放電特性および低温における放電特性を確保し．かつ比容量が高い非水電解質二次電池の実現を可能にしたものである。

【００１４】

【発明の実施の形態】本発明の請求項１に記載の発明は．正極と負極とこれらの間に配されるセパレータを備え．前記負極は．充電および放電によりリチウムイオンがインターカレーションおよびディインターカレーションを可逆的に繰り返すことができる負極材料として、

（１）広角Ｘ線回折法による（００２）面の面間隔（ｄ００２）が３．３７Å未満でかつＣ軸方向の結晶子の大きさ（Ｌｃ）が少なくとも１０００Å以上

（２）アルゴンイオンレーザーラマンスペクトルにおける１５８０ｃｍ$^{-1}$のピーク強度に対する１３６０ｃｍ$^{-1}$のピーク強度比であるＲ値が０．３以下でかつ１５８０ｃｍ$^{-1}$ピークの半値幅が２４ｃｍ$^{-1}$以下

（３）平均粒径が１０～３０μｍでかつ一番薄い部分の厚みが少なくとも３μｍ以上平均粒径以下

（４）ＢＥＴ法による比表面積が３．５ｍ^{2}／ｇ以上１０．０ｍ^{2}／ｇ以下

（５）タッピング密度が０．５ｇ／ｃｃ以上１．０ｇ／ｃｃ以下

（６）広角Ｘ線回折法による（１１０）／（００４）のＸ線回折ピーク強度比が０．０１５以上の特性を示す塊状の黒鉛粉末を核とし、その核の表面に炭素前駆体を被覆後．不活性ガス雰囲気下で７００～２８００℃の温度範囲で焼成し．炭素質物の表層を形成させた複層構造の炭素質粉末を用いた非水電解質二次電池にすることにより．リチウムイオン二次電池の諸特性を改善するとともに．高エネルギー密度化を達成し得るものである。

【００１５】上記（１）～（６）の特性を有する塊状黒鉛粒子は高純度で、かつ高結晶性の天然又は人造の鱗状又は鱗片状黒鉛を角取り的粉砕や割断的粉砕、球状化粉砕後篩分けの過程で黒鉛粉末の厚さが大きいもの．すなわち鱗片状粒子のなかでも球形に近いものを集めることにより、徒らに比表面積を増大させず．タッピング密度が０．５以上の粒子を得ることができる。またこの時の広角Ｘ線回折法による（１１０）／（００４）のＸ線回折ピーク強度比が０．０１５以上を示すものが良く、さらに平均円形度（粒子面積相当円の周囲長を分子とし、撮像された粒子投影像の周囲長を分母とした比率で、粒子像が真円に近いほど１となり、粒子像が細長いあるいはデコボコしているほど小さい値になる）は０．９４０以上と形状ファクターとしては球状化しているものが良い。一例として流体エネルギー粉砕機により鱗片状黒鉛粒子をさらに微粉砕する過程で、角取りしてディスク状またはタブレット状粒子に粉砕後篩分けする方法があげられるが、上記（１）～（６）の物性を示す黒鉛粒子であれば作成方法は特に限定されるものではない。

【００１６】上記黒鉛粉末の平均粒径が１０～３０μｍが好適に用いられるが、１２～２６μｍがより好ましく．１５～２３μｍが最も好ましい。この時、粒径１０μｍ未満の粉末の含有率を２０％以下．好ましくは１０％以下、又は粒径２５μｍを越える粉末の含有率を２０％以下、好ましくは１０％とすると更に好ましい。更に粒径１０μｍ未満および粒径２５μｍを越える粉末の含有率がそれぞれ２０％以下．好ましくは１０％以下および２０％以下．好ましくはそれぞれ１０％以下とすると最も好ましい。ＢＥＴ法による比表面積は３．５～１０．０ｍ^{2}／ｇの範囲のものを用いることができるが、４．０～８．０ｍ^{2}／ｇが好ましく．４．０～７．０ｍ^{2}／ｇが最も好ましい。

【００１７】リチウムイオンがインターカレーションされて生成する層間化合物のＣ$_{6}$Ｌｉを基準にした炭素１ｇ当たりの容量の理論値は３７２ｍＡｈであるが．このようにして選定した黒鉛粒子は、充放電レートを０．２ｍＡ／ｃｍ^{2}とした、リチウム金属対極を用いた半電池による電気容量測定を行い．比容量が３３０ｍＡｈ／ｇ以上．より好ましくは３５０ｍＡｈ／ｇ以上と上記理論容量に近ければ近いものほど好適に用いられる。

【００１８】本発明で用いることのできる黒鉛粒子核表面を被覆するための炭素前駆体としてはまず、液相で炭素化を進行させる有機物として、軟ピッチから硬ピッチまでのコールタールピッチ．石炭液化油等の石炭系重質油．アスファルテン等の直流系重質油．原油、ナフサなどの熱分解時に副生するナフサタール等分解系重質油等の石油系重質油．分解系重質油を熱処理することで得られる．エチレンタールピッチ、ＦＣＣデカントオイル、アシュランドピッチなど熱処理ピッチ等を用いることができる。さらにポリ塩化ビニル、ポリビニルアセテート．ポリビニルブチラール．ポリビニルアルコール等のビニル系高分子と３－メチルフェノールフォルムアルデヒド樹脂、３．５－ジメチルフェノールフォルムアルデヒド樹脂等の置換フェノール樹脂、アセナフチレン、デカシクレン、アントラセンなどの芳香族炭化水素．フェナジンやアクリジンなどの窒素環化合物、チオフェンなどのイオウ環化合物などの物質があげられる。また、固相で炭素化を進行させる有機物としては、セルロースなどの天然高分子．ポリ塩化ビニリデンやポリアクリロニトリルなどの鎖状ビニル樹脂、ポリフェニレン等の芳香族系ポリマー．フルフリルアルコール樹脂、フェノールーホルムアルデヒド樹脂．イミド樹脂等熱硬化性樹脂やフルフリルアルコールのような熱硬化性樹脂原料などがあげられる。これらの有機物を必要に応じて、適宜溶媒

を選択して溶解希釈することにより、黒鉛粒子核の表面に付着させ、使用することができる。

【0019】本願発明においては、通常、かかる黒鉛粒子核と炭素前駆体を混合したものを加熱し中間物質を得て、その後炭化焼成、粉砕することにより、最終的に黒鉛粒子核の表面に炭素質物の表層を形成させた複層構造の炭素質粉末を得るが、複層構造の炭素質粉末中の炭素質物の割合は50重量%以下0.1重量%以上、好ましくは25重量%以下0.5重量%以上、更に好ましくは15重量%以下1重量%以上、特に好ましくは10重量%以下2重量%以上となるように調整する。

【0020】一方、本願発明のかかる複層炭素質物を得るための製造工程は以下の4工程に分けられる。

【0021】第1工程

黒鉛粒子と炭素前駆体、更に必要に応じて溶媒とを種々の市販の混合機や混練機等を用いて混合し、混合物を得る工程。

【0022】第2工程

必要に応じ前記混合物を攪拌しながら加熱し、溶媒を除去した中間物質を得る工程。

【0023】第3工程

前記混合物又は中間物質を、窒素ガス、炭酸ガス、アルゴンガス等の不活性ガス雰囲気下で700℃以上2800℃以下に加熱し、炭素化物質を得る工程。

【0024】第4工程

前記炭素化物質を必要に応じて粉砕、解砕、分級処理など粉体加工する工程。

【0025】これらの工程中第2工程及び第4工程は場合によっては省略可能であり、第4工程は第3工程の前に行ってもよい。

【0026】また、第3工程の加熱処理条件としては、熱履歴温度条件が重要である。その温度下限は炭素前駆体の種類、その熱履歴によっても若干異なるが通常700℃以上、好ましくは900℃以上である。一方、上限温度は基本的に黒鉛粒子核の結晶構造を上回る構造秩序を有しない温度まで上げることができる。従って熱処理の上限温度としては、通常2800℃以下、好ましくは2000℃以下、更に好ましくは1500℃以下が好ましい範囲である。このような熱処理条件において、昇温速度、冷却速度、熱処理時間などは目的に応じて任意に設定する事ができる。また、比較的低温領域で熱処理した後、所定の温度に昇温する事もできる。なお、本工程に用いる反応機は回分式でも連続式でも又、一基でも複数基でもよい。

【0027】このようにして炭素質物の表層を形成させた本願発明の複層構造の炭素質粉末材料は、ラマンスペクトル分析によるピーク強度比R値や、X線広角回折の回折図において得られるd002、Lcの値において、核となる黒鉛材料の結晶化度を上回らないこと、すなわちR値は核のその値以上で、半値幅Δνは、核のその値

以上、d002値は、核のその値以上で、Lcは核のその値以下であることが好ましい。具体的な複層構造の炭素質粉末材料のR値としては、0.01以上1.0以下、好ましくは0.05以上0.8以下、より好ましくは0.1以上0.6以下、さらに好ましくは0.2以上0.4以下の範囲で、かつ、核の値以上であることが挙げられる。また、平均粒径が11～40μmのものが好適に用いられるが、13～30μmがより好ましく、16～25μmが最も好ましい。この時、粒径10μm未満の粉末の含有率を20%以下、好ましくは10%以下、又は粒径25μmを越える粉末の含有率を20%以下、好ましくは10%以下とすると更に好ましい。更に粒径10μm未満および粒径25μmを越える粉末の含有率がそれぞれ20%以下、好ましくは10%以下および20%以下、好ましくはそれぞれ10%以下とすると最も好ましい。また、粒子の一番薄い部分の厚さの平均値が4μm以上平均粒径以下であるものが好ましい。更にBET法による比表面積が1.0～5.0m^2/g、より好ましくは1.5～4.0m^2/g、更に好ましくは2.0～3.5m^2/gのものが好適に用いられる。複層構造の炭素質粉末材料のタッピング密度は炭素被覆により使用した該黒鉛材料よりも更に向上するが、0.7～1.2g/ccの範囲に制御することが望ましい。このような範囲に入る炭素質粉末をバインダーや各種添加剤とともに混合し、銅やニッケル等の集電体上に塗布や圧着などの方法により電極として使用できるよう成形する。そののち、平板プレスやロールプレス等で圧延することにより電極上の活物質層の密度（以下極板密度と呼ぶ）を調整する。この時、極板密度を1.2より大きく1.6以下とすることにより、より好ましくは1.3以上1.5以下とすることにより電池の低温放電時や高率放電時の電池容量を低下させることなく、電池の単位体積当たりの容量を最大に引き出すことができるようになる。このようにして作成した負極と通常使用されるリチウムイオン電池用の金属カルコゲナイド系正極を組み合わせて構成した電池は、4V級の高電圧を実現でき、かつ、容量が大きく、初期サイクルに認められる不可逆容量が小さく、高温下での放置における電池の保存性および信頼性が高く、高率放電特性及び低温における放電特性に極めて優れる。この場合のカルコゲナイド系正極はLi_xMO_2（Mは1種以上の遷移金属、x=0～1.2）が好適であり、特に、Li_xCoO_2、Li_xNiO_2、$Li_xMn_2O_4$および、それらのCo、Ni、Mnの一部を他の遷移金属などの元素で置換したものが好適である。

【0028】本発明は特に電解液を限定するものではないが、上記4V級正極と本発明の負極を用いた電池に用いられる電解液の溶媒としては耐酸化性及び低温特性に優れるエチレンカーボネート、プロピレンカーボネート、ブチレンカーボネートなどの環状カーボネート1種

以上と、ジメチルカーボネート、ジエチルカーボネート、エチルメチルカーボネートなどの鎖状カーボネート1種以上との混合溶媒を主成分とするのが好適である。また、必要に応じて、脂肪族カルボン酸エステルやエーテル類などの他の溶媒を混合できる。混合比率は、体積換算で環状カーボネートが溶媒全体の5～50%特に15～40%、鎖状カーボネートが10～90%、特に20～80%の範囲が好ましい。

【0029】また、正極に3V級などの比較的低電位の材料を使用する場合は、上記溶媒以外の溶媒も使用できる。

【0030】これらの溶媒の溶質にはリチウム塩が使用される。一般的に知られているリチウム塩には$LiClO_4$、$LiBF_4$、$LiPF_6$、$LiAlCl_4$、$LiSbF_6$、LiSCN、LiCl、$LiCF_3SO_3$、$LiCF_3CO_2$、$Li(CF_3SO_2)_2$、$LiAsF_6$、$LiN(CF_3SO_2)_2$などがある。

【0031】上記以外の電池構成上必要な部材の選択については何ら制約を設けるものではない。

【0032】上記炭素質物の表層を形成させた複層構造の炭素質粉末材料を負極として用いた電池は、炭素質物の表層を形成させない黒鉛粒子や上記（1）～（6）の特性を有しない黒鉛粒子を用いて炭素質物の表層を形成させた複層構造の炭素質粉末材料を負極として用いた電池に比べ、高率充放電性能および低温での高率放電性能を向上する。その上、高温下でも電解液中の有機溶媒を分解させ難く、セル内圧の上昇をさせ難くなるため従来問題であった電解液の漏液事故を防ぐことができる。また、複層構造の炭素質粉末にすることで比表面積が小さくなるため、高温下でも電解液中の有機溶媒を分解させ難く、高温での電池性能の劣化を小さくすることができる。

【0033】

【実施例】以下、本発明の実施形態について、図表を用いて詳細に説明する。

【0034】（測定法）

（1）体積基準平均粒径

界面活性剤にポリオキシエチレン（20）ソルビタンモノラウレートの2vol%水溶液を約1cc用い、これを予め炭素質粉末に混合し、しかる後にイオン交換水を分散媒として、堀場製作所社製レーザー回折式粒度分布計「LA-700」にて、体積基準平均粒径（メジアン径）を測定した。

【0035】（2）タッピング密度

（株）セイシン企業社製粉体密度測定器「タップデンサー KYT-3000」を用い、サンプルが透過する篩には、目開き300μmの篩を使用し、20ccのタッピングセルに粉体を落下させ、セルが満杯に充填された後、ストローク長10mmのタッピングを1000回行って、その時のタッピング密度を測定した。

【0036】（3）BET比表面積測定

大倉理研社製AMS-8000を用い、予備乾燥として350℃に加熱し、15分間窒素ガスを流した後、窒素ガス吸着による相対圧0.3におけるBET1点法によって測定した。

【0037】（4）X線回折

試料に対して約15%のX線標準高純度シリコン粉末を加えて混合し、試料セルに詰め、グラファイトモノクロメーターで単色化したCuKα線を線源とし、反射式ディフラクトメーター法によって、広角X線回折曲線を測定した。測定により得られた広角X線回折曲線を学振法に基づき、（002）面の面間隔（d002）およびC軸方向の結晶子の大きさ（Lc）を測定した。

【0038】（5）ラマン測定

日本分光社製NR-1800を用い、波長514.5nmのアルゴンイオンレーザー光を用いたラマンスペクトル分析において、1580cm^{-1}の付近のピークPAの強度IA、1360cm^{-1}の範囲のピークPBの強度IBを測定し、その強度の比R=IB/IAを測定した。また、1580cm^{-1}の付近のピークPAの半値幅を波数（cm^{-1}）を単位として求めた。試料の調製にあたっては、粉末状態のものを自然落下によりセルに充填し、セル内のサンプル表面にレーザー光を照射しながら、セルをレーザー光と垂直な面内で回転させて測定を行った。

【0039】（6）炭素粉末の一番薄い部分の厚さの平均値

炭素粉末の厚さの平均値は、各供試黒鉛粉末を金型を用い加圧成形した後、成型体を加圧方向と平行に切断した面のSEM像から求めた。すなわち、炭素粉末の一番薄い部分の厚さ方向の値を100個以上測定し、その平均値を求めた。

【0040】（7）（110）/（004）のX線ピーク強度比の測定

（110）/（004）のX線ピーク強度比は金型を用い、炭素粉末を加圧し、密度約1.7g/ccのペレット状に成形し、広角X線回折測定により得られる（110）/（004）のピーク強度比を算出し、その平均値を求めた。（004）面と（110）面の回折線は黒鉛結晶の炭素六員環網状平面並びにその垂直面での回折線である。鱗片形状の多い場合、ディスク状またはタブレット状の黒鉛粒子が多い場合に比べて、ペレット作成時に加圧面と平行方向に黒鉛粒子が選択的に配向する。従って、ディスク状またはタブレット状の黒鉛粒子に比べて鱗片状粒子が多くなると（110）/（004）ピーク強度比は小さくなる。

【0041】（8）平均円形度の測定

東亜医用電子社製フロー式粒子像分析装置「FPIA-1000」を使用し、水に分散した黒鉛粒子をCCDカメラで1/30秒ごとに撮像し、その粒子像をリアルタ

イム解析することにより全粒子に対する平均円形度の算出を行った。分散媒にはイオン交換水を使用し．界面活性剤には、ポリオキシエチレン（２０）ソルビタンモノラウレートを使用した。平均円形度とは、粒子投影面積相当円の周囲長を分子とし．撮像された粒子投影像の周囲長を分母とした比率で．粒子像が真円に近いほど１となり．粒子像が細長いあるいはデコボコしているほど小さい値になる。

【００４２】（基礎実験例１）図１はリチウムイオン二次電池の負極の可逆容量および不可逆容量を測定するためのコイン形セルの断面図である。図１において．ステンレス鋼製セルケース１の内底面にステンレス鋼製のエキスパンドメタルからなるグリッド３を予めスポット溶接しておき、このグリッド３とリチウムイオン二次電池の負極用炭素粉末を主成分とする合剤を缶内成型法により炭素電極５として一体に固定する。炭素電極５の合剤は．供試用炭素粉末とアクリル系結着剤とを重量比で１００：５の比率で混合したものである。ステンレス鋼製のふた２の周縁には、ポリプロピレン製ガスケット７が嵌着されており．かつ、ふた２の内面には金属リチウム４が圧着されている。炭素電極５に非水電解質を注加含浸させた後、微孔性ポリエチレン膜からなるセパレータ６を介してガスケット７付のふた２をセルケース１にカップリングし．セルケース１の上縁開口部を内方向にカールさせて封口する。なお．非水電解質としては．エチレンカーボネートとジエチルカーボネートとの体積比

１：１の混合溶媒に六フッ化リン酸リチウムを１ｍｏｌ／１の濃度に溶解させた有機電解液を用いた。炭素電極５に１４種類の供試炭素粉末を用いてセルを作製し、炭素電極５を正極．金属リチウム電極４を負極として、２０℃のもとで電流密度０．３ｍＡ／ｃｍ² の定電流で充電および放電する。セル電圧が０Ｖになるまで炭素にリチウムをインターカレートした後、セル電圧が１．０Ｖになるまで炭素からリチウムをディインターカレートして求めた量を可逆容量とする。インターカレートに要した電気量から可逆容量を除した値を不可逆容量とした。なお．これらテストセルの充放電終止電圧値は．負極炭素／正極ＬｉＣｏＯ₂ 系の実用電池の充電終止電圧４．２０Ｖおよび放電終止電圧２．７５Ｖにほぼ相当する。

【００４３】常法により粉砕して得られる鱗片状人造黒鉛．天然黒鉛および種々の粉砕方法によりタッピング密度を向上させた人造及び天然黒鉛粉末（試料Ｎｏ．１～１５）およびそれらとの比較試料として、特開平７－１３４９８８号公報に開示されているメソカーボンマイクロビーズを黒鉛化した球状のメソカーボンマイクロビーズ（ＭＣＭＢ．試料Ｎｏ．１６）および石油ピッチコークス粉末（試料Ｎｏ．１７）を負極用供試炭素粉末とし．それら粉末の物性値と前述した可逆容量と不可逆容量とを表１にまとめて示す。

【００４４】

【表１】

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試料No.	原材料	製造元	商品名	物性値									電気特性	
				d002 (Å)	Lc (Å)	ラマンR値	ラマン半値幅 (cm^{-1})	平均粒径 (μm)	比表面積 (m^2/g)	吸油量 平均粒さ (μm)	タッピング密度 (g/cc)	平均円形度	(110)/(004)	可逆容量 (mAh/g)	不可逆容量 (mAh/g)
1	人造黒鉛	ティムカル	KS15	3.36	1000以上	0.16	21.1	7.8	14.5	1.1	0.32	0.928	0.008	351	53
2	人造黒鉛	ティムカル	KS25	3.36	1000以上	0.16	21.4	10.1	11.9	1.3	0.40	0.925	0.009	353	43
3	人造黒鉛	ティムカル	KS44	3.36	1000以上	0.15	22.2	16.8	9.3	1.8	0.41	0.919	0.010	359	36
4	人造黒鉛	ティムカル	KS75	3.36	1000以上	0.15	22.2	23.7	7.2	2.1	0.44	0.918	0.011	353	35
5	人造黒鉛	日本黒鉛	SP-10	3.35	1000以上	0.18	21.2	32.5	6.9	2.4	0.41	0.927	0.012	353	32
6	人造黒鉛	日本黒鉛	SP-20	3.36	1000以上	0.15	24.0	14.9	8.7	1.8	0.23	0.937	0.010	356	40
7	天然黒鉛	エスイーシー	SNO10	3.35	1000以上	0.19	20.9	10.4	8.7	2.0	0.46	0.919	0.008	362	39
8	天然黒鉛	エスイーシー	SNO15	3.35	1000以上	0.17	21.5	12.9	7.8	2.3	0.46	0.927	0.009	361	35
9	天然黒鉛	エスイーシー	SNO20	3.36	1000以上	0.16	21.6	18.7	6.8	2.5	0.48	0.930	0.009	358	34
10	天然黒鉛	日本黒鉛	ACP-20NB	3.36	1000以上	0.18	21.6	19.0	4.9	5.4	0.64	0.947	0.038	354	23
11	天然黒鉛	日本黒鉛	ASP-20NB	3.36	1000以上	0.17	21.1	16.7	4.9	6.3	0.66	0.943	0.039	357	20
12	人造黒鉛	日本黒鉛	SP-20NB	3.36	1000以上	0.20	20.9	15.7	6.6	3.5	0.61	0.942	0.032	360	26
13	天然黒鉛	中越黒鉛	H-0	3.36	1000以上	0.21	22.0	22.3	3.6	5.6	0.55	0.940	0.035	358	24
14	天然黒鉛	中越黒鉛	H-1	3.36	1000以上	0.18	21.8	18.4	5.8	6.5	0.79	0.941	0.038	355	24
15	天然黒鉛	中越黒鉛	H-2	3.36	1000以上	0.24	22.1	17.7	6.4	5.8	0.70	0.940	0.039	336	26
16	人造黒鉛	大阪ガス	MCMB	3.37	700	0.19	23.4	5.3	2.9	5.3	1.10	0.966	0.120	295	18
17	人造黒鉛	日本黒鉛	GMW-20NB	3.37	750	0.32	23.0	17.2	5.3	8.1	0.95	0.961	0.110	298	27

【００４５】表１の結果からＬｃが１０００Ａ未満である比較試料の球状黒鉛粉末（試料Ｎｏ．１６）およびコークス粉末（試料Ｎｏ．１７）は、不可逆容量は比較的小さいが、エネルギー密度に大きく影響する可逆容量はどちらも３００ｍＡｈ／ｇ未満と小さかった。これらに対して、原材料が天然黒鉛および人造黒鉛粉末の試料Ｎｏ．１～１５の可逆容量はすべて少なくとも３５０ｍＡｈ／ｇで、比容量の理論値（３７２ｍＡｈ／ｇ）に近似した値となった。これらのなかで、試料Ｎｏ．１０～１５の黒鉛粉末の不可逆容量は２０～２６ｍＡｈ／ｇで、他の黒鉛粉末（試料Ｎｏ．１～９）のそれより小さいことが注目される。

【００４６】本発明の前提条件として広角Ｘ線回折による（００２）面の面間隔（ｄ００２）が３．３７Ａ未満であり、Ｃ軸方向の結晶子の大きさ（Ｌｃ）が少なくとも１０００Ａ以上である結晶化度および純度が高い天然黒鉛または人造黒鉛をリチウムイオン二次電池の負極材に用いることより高水準の可逆容量が得られることが理解される。

【００４７】（基礎実験例２）基礎実験例１で．可逆容量および不可逆容量を求めた負極用炭素粉末（試料Ｎｏ．１～１７）を用いて．円筒形セルを作製し．低温に

おける高率放電特性および充電状態で高温放置した場合の漏液性を測定した。

【0048】図2は渦巻状電極群構成の円筒形セルの断面図である。図2において．各1枚の帯状正極10と負極11とを微孔性ポリエチレン膜からなるセパレータ12を介して渦巻状に捲回して電極群が構成される。正極10は活物質材料のリチウムとコバルトとの複合酸化物である$LiCoO_2$と導電材のカーボンブラックと結着剤のポリ四フッ化エチレン（PTFE）とを重量比で100：3：10の割合で混合したペーストを集電体であるアルミニウム箔の両面に塗着、乾燥後ロールプレスし．所定寸法に裁断したものである。なお、結着剤のPTFEはディスパージョン溶液のものを用いた。正極10のアルミニウム箔には．正極リード片13がスポット溶接されている。負極11は供試炭素粉末にアクリル系結着剤溶液を加えて混合したペーストを集電体である銅箔の両面に塗着．乾燥後ロールプレスし、所定の寸法に裁断したものである。負極11の銅箔には負極リード片14がスポット溶接されている。捲回した電極群の下面に底部絶縁板15を装着して、ニッケル鍍銅板製のセルケース16内に収容した後．負極リード片14をセルケース16の内底面にスポット溶接する。その後電極群上に上部絶縁板17を載置してからセルケース16の開口部の所定位置に消入れし．所定量の有機電解液を注入含浸させる。有機電解液としては基礎実験例1と同じ有機電解液を用いた。その後．周縁にガスケット18が嵌着

された封口板19の内底面に正極リード片13をスポット溶接する。封口板19をセルケース16の開口部にガスケット18を介して嵌め込んで、セルケース16の上縁を内方向にカールして封口すればセルは完成する。

【0049】各セルの放電容量は負極容量で規制されるようにし、種類にかかわらず各セルの負極用炭素粉末量を同じにした。他の部品材料の使用量、作製方法は全く同じにして負極用炭素粉末の比較ができるようにした。

【0050】17種類の負極用炭素粉末を用いたセルA～Q各5セルについて、20℃ですべてのセルを100mA（1／5C）定電流で各セルの端子電圧が4．2Vになるまで充電した後、100mA（1／5C）定電流で2．75Vまで放電して．1／5C放電容量を求めた。その後、同様に充電した後500mA（1C）定電流で2．75Vまで放電して、1C放電容量を求めた。次いで、20℃で充電した後、－20℃で24時間放置し．同じ－20℃で1C放電容量を求めた。各セルを20℃に静置し．セルの温度が20℃に復してから同じ電池で充電した後．100℃で1日放置し、セルの温度が20℃になってから漏液の有無を全セルについて観察した。

【0051】供試炭素粉末の物性値に対比して．前述した電池性能（5セルの平均値）をまとめて表2に示す。

【0052】

【表2】

試料 No.	原材料	製造元	品名	セル記号	電池性能			
					1/5C 放電持続	1C 放電容量	-20℃1C 放電容量	高温放置後 漏液数
1	人造黒鉛	ティムカル	KS15	A	511	501	450	5/5
2	人造黒鉛	ティムカル	KS25	B	532	523	452	3/5
3	人造黒鉛	ティムカル	K344	C	539	521	410	2/5
4	人造黒鉛	ティムカル	KS35	D	549	508	359	0/5
5	人造黒鉛	日本黒鉛	SP-10	E	537	483	367	1/5
6	人造黒鉛	日本黒鉛	SP-20	F	541	528	433	2/5
7	天然黒鉛	エスイーシー	SNO10	G	538	522	473	3/5
8	天然黒鉛	エスイーシー	SNO15	H	545	531	452	2/5
9	天然黒鉛	エスイーシー	SNO20	I	536	520	407	1/5
10	天然黒鉛	日本黒鉛	ACP-20NB	J	554	543	421	0/5
11	天然黒鉛	日本黒鉛	ASP-20NB	K	561	550	445	0/5
12	人造黒鉛	日本黒鉛	SP-20NB	L	557	546	440	0/5
13	天然黒鉛	中越黒鉛	H-0	M	553	541	420	0/5
14	天然黒鉛	中越黒鉛	H-1	N	554	543	440	0/5
15	天然黒鉛	中越黒鉛	H-2	O	560	548	445	0/5
16	人造黒鉛	大阪ガス	MCMB	P	478	463	417	0/5
17	人造黒鉛	日本黒鉛	GMW-20NB	Q	485	468	372	0/5

【００５３】表２から、表１で示した可逆容量が小さかった試料Ｎｏ．１６および１７の２０℃での１／５Ｃおよび１Ｃ放電容量は低いが．試料Ｎｏ．１～１５の黒鉛粉末のそれらは相対的に大きい。しかしながら試料Ｎｏ．１～１５の内で、低温における高率放電容量（－２０℃．１Ｃ）が４００ｍＡ以上を示したのは、試料Ｎｏ．１、２、３．６、７．８、９、１０、１１．１２、１３．１４、および１５の黒鉛粉末によるセルＡ．Ｂ、Ｃ．Ｆ、Ｇ、Ｈ．Ｉ、Ｊ．Ｋ、Ｌ、Ｍ．Ｎ、およびＯであった。さらに．高温放置後に漏液が全く認められなかったのは、試料Ｎｏ．４．１０、１１．１２、１３、１４．１５、１６．および１７の炭素粉末によるセルＤ、Ｊ．Ｋ、Ｌ、Ｍ．Ｎ、Ｏ．Ｐ、およびＱであった。これらの結果からすべての電池性能にわたって優れていたのは試料Ｎｏ．１０、１１．１２、１３．１４および１５の黒鉛粉末によるセルＪ．Ｋ、Ｌ、Ｍ．ＮおよびＯであった。

【００５４】（実施例及び比較例）基礎実験例２で１／５Ｃ放電容量．１Ｃ放電容量、－２０℃での１Ｃ放電容量および高温下で放置した場合の漏液性を測定したセルで．すべての電池特性にわたって優れていた試料Ｎｏ．１０、１１、１２、１３．１４および１５の黒鉛粉末に

よるセルＪ、Ｋ．Ｌ、Ｍ．Ｎおよび○の電池を高温下で放置した後、基礎実験例２に記載した充放電条件で２０℃での１／５Ｃ放電容量を求めたところ、高温下で放置する前の１／５Ｃ放電容量に比べ、７０～８０％の放電容量しか示さなかった。これらのセルは、高温下での放置による漏液事故は皆無であり、電池の信頼性は向上したものの、電池特性の劣化が激しく．高温下に放置された場合においても、電池特性の劣化を小さくする必要がある。

【００５５】そこで、基礎実験例２で電池性能を測定した負極用炭素粉末（試料Ｎｏ．１～１７）をそれぞれ核として、ナフサ分解時に得られる石油系タールピッチを炭素前駆体として用いて炭素化後５重量％になるよう被覆後．不活性ガス流の下．最終的に１２００℃で熱処理

した。その後．室温まで冷却後、粉砕機を用いて解砕し．一定の粒径分布をもった炭素系複合粉末を得た。こうして核の表面上に新しい炭素質物の表層を形成させた複層構造の炭素質粉末（試料Ｎｏ．１８～３４）を作成し．負極用供試炭素粉末とした。

【００５６】１７種類の負極用炭素粉末を用いた以外、基礎実験例２と同様にそれぞれセルＲ～ＡＨ各５セル作製し．同様の電池性能を測定したのに加えて、高温放置後漏液が見られなかったセルの１／５Ｃ放電容量を測定した。

【００５７】供試炭素粉末の物性値に対して前述した電池性能をまとめて表３に示す。

【００５８】

【表３】

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試料No.	素材試料No.	原材料	製造元	商品名	粉末物性値					セル記号	電池性能					
					平均粒径 (μm)	比表面積 (m²/g)	表面部平均厚さ (μm)	タッピング密度 (g/cc)			1/5C放電容量 (mAh)	1C放電容量 (mAh)	-20℃ 1C放電容量 (mAh)	高温放置後の1C放電容量	高温放置前の1/5C放電容量 (mAh)	高温放置前の1/5C放電容量比 (%)
18	1	人造黒鉛	ティムカル	KS15	12.0	4.9	1.9	0.47	R	520	513	448	4/5	-	-
19	2	人造黒鉛	ティムカル	KS25	12.4	4.5	2.4	0.57	S	542	530	434	2/5	-	-
20	3	人造黒鉛	ティムカル	KS44	17.7	4.2	2.6	0.61	T	549	532	411	1/5	-	-
21	4	人造黒鉛	ティムカル	KS15	23.2	3.1	3.1	0.74	U	553	520	337	0/5	455	82.3
22	5	人造黒鉛	日本黒鉛	SP-10	38.8	2.5	3.3	0.62	V	547	490	269	1/5	-	-
23	6	人造黒鉛	日本黒鉛	SP-20	22.9	4.8	2.7	0.57	W	549	535	434	2/5	-	-
24	7	天然黒鉛	エスイーシー	SNO10	18.6	4.1	3.1	0.82	X	541	530	475	2/5	-	-
25	8	天然黒鉛	エスイーシー	SNO15	21.4	3.7	3.2	0.81	Y	554	537	432	1/5	-	-
26	9	天然黒鉛	エスイーシー	SNO20	25.2	2.9	3.4	0.83	Z	542	528	409	1/5	-	-
27	10	天然黒鉛	日本黒鉛	ACP-20NB	20.2	2.6	8.1	0.81	AA	566	552	423	0/5	531	93.8
28	11	天然黒鉛	日本黒鉛	ASP-20NB	21.4	2.8	10.2	0.88	AB	569	559	447	0/5	534	93.8
29	12	人造黒鉛	日本黒鉛	SP-20NB	21.5	2.8	4.9	0.70	AC	567	549	443	0/5	532	93.8
30	13	天然黒鉛	中越黒鉛	H-D	24.8	2.3	7.6	0.85	AD	560	550	425	0/5	530	94.6
31	14	天然黒鉛	中越黒鉛	H-1	24.0	2.4	10.5	0.94	AE	561	552	438	0/5	532	94.8
32	15	天然黒鉛	中越黒鉛	H-2	21.2	2.6	8.3	0.92	AF	563	557	462	0/5	537	95.4
33	16	人造黒鉛	大阪ガス	MCMB	6.5	1.8	6.1	1.26	AG	485	370	415	0/5	450	92.8
34	17	人造黒鉛	日本黒鉛	GMW-20NB	17.2	1.6	8.7	1.05	AH	487	473	374	0/5	452	92.8

【0059】表3から、複層構造の炭素質粉末にすることによる1／5C放電容量．1C放電容量、－20℃1C放電容量の変化は見られなかった。しかしながら、基礎実験例2で漏液が見られた試料No．1．2．3．5．6、7、8および9を核にした複層構造の炭素質粉末試料（No．18、19．20、22、23．24、25．26）によるセルR．S、T．V、W、X．Y、Zの漏液数は減少する傾向を示したが．漏液を止めるには不十分であった。一方．高温放置後に漏液が全く認められなかったのは、試料21、27．28、29．30．31、32．33および34の複層構造の炭素質粉末によるセルU．AA、AB、AC．AD、AE．AF．AGおよびAHであった。これらのセルの高温放置後の1／5C放電容量は．高温放置前の1／5C放電容量に対して82～96%の値となり．複層構造の炭素質粉末にすることで高温放置後の1／5C放電容量は向上した。これらのなかで、試料27、28、29．30、31および32の複層構造の炭素質粉末によるセルAA．AB、AC．AD、AEおよびAFは、高温放置後の1／5C放電容量はすべてすくなくとも530mAh以上で、高温放置前の1／5C放電容量に対して93%以上の値となった。これらの結果からすべての電池性能

にわたって優れていたのは試料Ｎｏ．２７、２８．２９．３０、３１および３２の複層構造の炭素質粉末によるセルＡＡ、ＡＢ、ＡＣ．ＡＤ、ＡＥおよびＡＦであった。

【００６０】なお、上記において複層構造の炭素質粉末を得るために焼成温度を１３００℃で実施したが．７００℃～２８００℃の温度範囲で、同様の粉末物性が得られ．本発明と同様の効果が見られた。また、複層構造の炭素質粉末は．核に用いた黒鉛粉末と新たに表層を形成させた炭素物質との重量比が９５：５になるように、核材料とピッチを混合し作製したが、これらの重量比が９９：１～５０：５０の範囲で同様の物性が得られ．本発明と同様の効果が得られた。

【００６１】また、上記においては．本発明について非水電解液として有機電解液についてのみ説明したが、ポリマーなどの陽イオン伝導性固体電解質からなる二次電池に適用することを妨げるものではない。

【００６２】

【発明の効果】以上のように本発明による負極用黒鉛粉末を使用することにより．比容量の理論値（３７２ｍＡｈ／ｇ）の少なくとも９５％の３５４～３６０ｍＡｈ／ｇ（９５．２～９６．８％）であり．不可逆容量は２０～２６ｍＡｈ／ｇと小さく．エネルギー密度の向上に資するものである。さらに．高率充放電および低温高率放電性能が優れるだけでなく．高温放置によっても漏液亭故が発生せず．電池性能の劣化も小さな、信頼性の高い＊

＊リチウム二次電池を提供できるという効果を奏し得るものである。

【図面の簡単な説明】

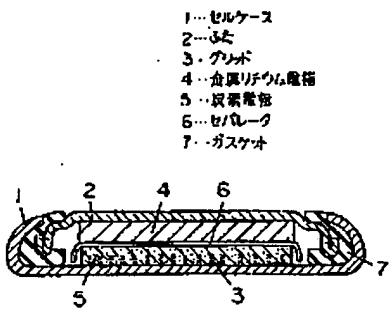
【図１】本発明の効果を検討すべく可逆容量および不可逆容量を測定するためのコイン形セルの断面図。

【図２】本発明の実施形態による渦巻状電極群構成の円筒形セルの断面図。

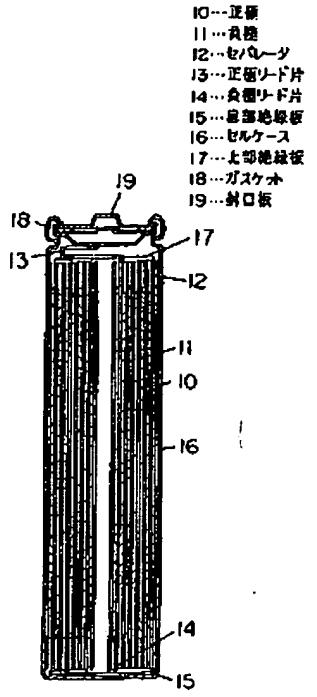
【符号の説明】

１：セルケース
２：ふた
３：グリッド
４：金属リチウム電極
５：炭素電極
６：セパレータ
７：ガスケット
１０：正極
１１：負極
１２：セパレータ
１３：正極リード片
１４：負極リード片
１５：底部絶縁板
１６：セルケース
１７：上部絶縁板
１８：ガスケット
１９：封口板

【図１】



【図２】



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(72)発明者　杉本　豊次
大阪府門真市大字門真1006番地　松下電器産業株式会社内

(72)発明者　山口　祥司
茨城県稲敷郡阿見町中央８丁目３番１号　三菱化学株式会社内筑波研究所内

(72)発明者　林　学
茨城県稲敷郡阿見町中央８丁目３番１号　三菱化学株式会社内筑波研究所内

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Country: **JP** Japan
Kind: **A**

Inventor: **KITAGAWA MASAKI;**
KOSHINA HIDE;
SUGIMOTO TOYOJI;
YAMAGUCHI SHOJI;
HAYASHI MANABU;

Assignee: **MATSUSHITA ELECTRIC IND CO LTD**
MITSUBISHI CHEM CORP
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Priority Number: 1997-05-30 **JP1997000141920**

Abstract:

PROBLEM TO BE SOLVED: To improve reliability of a lithium secondary battery and improve densification of high energy by using carbonaceous powder having a plural-layer structure that a surface layer of a carbonaceous material is formed by baking it under a specific condition after a surface of its nucleus is covered with a carbon precursor by using graphite powder having a specific property as a nucleus, as a negative electrode active material.

SOLUTION: Massive graphite powder has the following characteristic. Spacing of a (002) surface is less than 3.37 Å, and the size of a C axis directional crystallite is not less than 1000 Å. and the ratio of peak intensity of 1360 cm to peak intensity of 1580 cm-1 of a spectrum is not more than 0.3, and a half value width of a 1580 cm-1 peak is not more than 24 cm-1, and the average particle size is 10 to 30 μm, and a thickness of the thinnest part is 3 μm to the average particle diameter, and the specific surface area is 3.5 m2/g to 10.0 m2/g, and tapping density is 0.5 g/cc to 1.0 g/cc, and the X-ray diffraction peak intensity ratio of (110)/(004) is not less than 0.015. Baking to obtain a plural-layer carbonaceous material is performed in a temperature range of 700 to 2800°C in an inert gas atmosphere.

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INPADOC Legal Status: None Get N w: Family L gal Status Report

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CLAIMS

[Claim(s)]
[Claim 1] It has the separator allotted between a positive electrode, a negative electrode, and these. the aforementioned negative electrode As a negative-electrode material into which a lithium ion can repeat an intercalation and a day intercalation in reversible by charge and electric discharge The nonaqueous electrolyte rechargeable battery using the carbonaceous powder of the double layer structure in which used as the nucleus the massive graphite powder which shows the following properties, calcinated by the 700-2800-degree C temperature requirement under inert gas atmosphere after covering a carbon precursor on the front face of the nucleus, and the surface of a carbonaceous object was made to form. (1) Are based on a wide angle X-ray diffraction method. The spacing of a field (002) (d002) by less than 3.37A And the size of the microcrystal of C shaft orientations (Lc) At least 1000A or more (2) to an Ar-ion-laser Raman spectrum To the peak intensity of 1580cm-1 which can be set The R value which is the peak intensity ratio of receiving 1360cm-1 is 0.3 or less. the average of the thickness of the portion with the thinnest 1580cm-1 full width at half maximum whose or less [24cm -] 1 (3) mean particle diameter is 10-30 micrometers Below at least 3-micrometer or more mean particle diameter (4) The X diffraction peak intensity ratio of/(004) according [10.0m2 / below g(5) tapping density] more than 3.5m2 / g in the specific surface area by the BET adsorption method to 0.5g/cc or more 1.0g[/cc] or less(6) wide-angle X-ray diffraction method (110) is 0.015 or more. [Claim 2] The nonaqueous electrolyte rechargeable battery according to claim 1 whose degree of mean-circle form of the graphite used for a nucleus is 0.940 or more.
[Claim 3] The nonaqueous electrolyte rechargeable battery according to claim 1 or 2 whose tapping density of the carbonaceous powder material of a double layer structure is 0.7g/cc or more 1.2g/cc or less.
[Claim 4] The nonaqueous electrolyte rechargeable battery according to claim 1 to 3 whose specific surface area by the BET adsorption method of the carbonaceous powder material of a double layer structure is 1.0-5.0m2 / g.
[Claim 5] The mean particle diameter of the carbonaceous powder material of a double layer structure is 11-40 micrometers, and the average of the thickness of the thinnest portion is a nonaqueous electrolyte rechargeable battery according to claim 1 to 4 below 4-micrometer or more mean particle diameter.
[Claim 6] the separator allotted between a positive electrode, a negative electrode, and these -- having -- the aforementioned positive electrode -- a lithium content oxide (a chemical formula LixMO2 --) M makes an active material one or more sorts of transition metals chosen from Co, nickel, Mn, and Fe, and 1.2 or less [x= 0 or more]. however, the aforementioned negative electrode As a negative-electrode material into which a lithium ion can repeat an intercalation and a day intercalation in reversible by charge and electric discharge The nonaqueous electrolyte rechargeable battery using the carbonaceous powder of the double layer structure in which used as the nucleus the massive graphite powder which shows the following properties, calcinated by the 700-2800-degree C temperature requirement under inert gas atmosphere after covering a carbon precursor on the front face of the nucleus, and the surface of a carbonaceous object was made to form.

(1) Are based on a wide angle X-ray diffraction method. The spacing of a field (002) (d002) by less than 3.37A And the size of the microcrystal of C shaft orientations (Lc) At least 1000A or more (2) to an Ar-ion-laser Raman spectrum To the peak intensity of 1580cm-1 which can be set The R value which is the peak intensity ratio of receiving 1360cm-1 is 0.3 or less. the average of the thickness of the portion with the thinnest 1580cm-1 full width at half maximum whose or less [24cm -] 1 (3) mean particle diameter is 10-30 micrometers Below at least 3-micrometer or more mean particle diameter (4) The X diffraction peak intensity ratio of/(004) according [10.0m2 / below g(5) tapping density] more than 3.5m2 / g in the specific surface area by the BET adsorption method to 0.5g/cc or more 1.0g[/cc] or less(6) wide-angle X-ray diffraction method (110) is 0.015 or more.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to a nonaqueous electrolyte rechargeable battery, especially relates to the carbon material for negative electrodes of a rechargeable lithium-ion battery.
[0002]
[Description of the Prior Art] Conventionally, as a nonaqueous electrolyte rechargeable battery, it aims at high-energy density-ization by the high voltage and high capacity, and the so-called lithium secondary battery using the organic electrolytic solution which consists of an organic-solvent solution of lithium salt as nonaqueous electrolyte, such as chalcogen compounds, for example, manganese dioxide, molybdenum disulfide, selenium-ized titanium, etc., such as the oxide and sulfide of transition metals, and a selenide, is examined as a metal lithium and a positive active material as a negative-electrode active material.
[0003] However, although this lithium secondary battery can choose the intercalation compound in which the charge-and-discharge property was comparatively excellent as a positive active material, the charge-and-discharge property of the metal lithium of a negative electrode is not necessarily excellent. Therefore, it was difficult to lengthen the cycle life which repeats charge and discharge, there was a possibility that generation of heat by the internal short circuit might moreover take place, and the problem was in safety. That is, the metal lithium of a negative-electrode active material is eluted as a lithium ion in the organic electrolytic solution by electric discharge. The eluted lithium ion has some which deposit as an activity shape [shape of arborescence or moss] metallic crystal by charge, without depositing flat and smooth altogether like origin although deposited on a negative-electrode front face as a metal lithium. The front face of the metallic crystal itself is being worn with a passive state coat, and is inactivated, and an activity metallic crystal stops being able to contribute it to electric discharge easily while decomposing the organic solvent in the electrolytic solution. Consequently, since negative-electrode capacity fell as the charge-and-discharge cycle progressed, negative-electrode capacity needed to be made remarkably larger than that of a positive electrode at the time of cell production. Moreover, an activity arborescence metal lithium crystal may penetrate separator, may contact a positive electrode, and may carry out an internal short circuit. By the internal short circuit, a cell has a possibility of generating heat.
[0004] Then, as a negative-electrode material, the so-called rechargeable lithium-ion battery using the carbon material which can repeat an intercalation and a day intercalation in reversible is proposed by charge and electric discharge, research and development is actively done, and the utilization stage is already greeted by them. Since an activity arborescence metal lithium crystal does not deposit on a negative-electrode front face at the time of charge and discharge unless this rechargeable lithium-ion battery is overcharged, improvement in safety can expect very much. Furthermore, since this cell excels remarkably the lithium secondary battery which uses a metal lithium for a negative-electrode active material in the high charge-and-discharge property and the cycle life, the need of this cell is elongated

quickly in recent years.
[0005] LiCoO2 which is equivalent to an electric discharge state as a positive active material of a 4V class rechargeable lithium-ion battery, LiNiO2, LiMnO2, and LiMn 2O4 etc. -- the multiple oxide of a lithium and transition metals is adopted or examined As an electrolyte, nonaqueous electrolyte, such as the organic electrolytic solution and a polymer solid electrolyte, is used like a lithium secondary battery.

[0006] When a graphite is used for negative-electrode material, the theoretical values of the capacity per 1g of carbon on the basis of C6 Li of the intercalation compound which the intercalation of the lithium ion is carried out and it generates are 372mAh(s). Therefore, in various carbon material, you should choose that to which the theoretical value of this amount of specific volume is approached, and it becomes high as much as possible as a negative electrode of a practical use cell, the capacity value (mAh/cc), i.e., the capacity density, per unit volume.
[0007] In the difficulty graphitized carbon commonly called a hard carbon among various carbon material, the material exceeding said amount theoretical value of specific volume (372 mAh/g) is found out, and examination is advanced. However, the true specific gravity of the amorphous carbon of difficulty graphitization nature is small, and since it is bulky, it is substantially difficult [it] to enlarge capacity density of a negative electrode. It cannot be said as **, so that the negative-electrode potential after charge moreover resembles metal lithium potential, but a discharge potential has many technical problems, like flat nature is also inferior.
[0008] On the other hand, since the potential after charge is approximated to metal lithium potential, and the flat nature of a discharge potential is also excellent and a charge-and-discharge property improves as a practical use cell when a natural graphite with high crystallinity and artificial-graphite powder are used for a negative electrode, recently, graphite system powder is becoming in use [negative-electrode material].
[0009] It is in it, and if the mean particle diameter of the graphite powder for negative electrodes of a rechargeable lithium-ion battery is large, there is an inclination for the charge-and-discharge property in high rate and the electric discharge property in low temperature to be inferior.
[0010] Then, if a powdered mean particle diameter is made small and a mean particle diameter will be made small too much at ** and others although a high charge-and-discharge property and a low-temperature electric discharge property improve, when a powdered specific surface area becomes large too much, the problem to which the irreversible capacity which the lithium inserted by the initial charge into powder cannot contribute to the electric discharge after the 1st cycle becomes large will arise. While this phenomenon was a fatal fault, when a cell was left to a high-energy density-ized intention under an elevated temperature which exceeds 100 degrees C, it makes the solvent in the organic electrolytic solution disassemble, has a possibility of it not only carrying out self-discharge, but raising cell internal pressure and causing liquid spill accident, and had become the cause of reducing the reliability of a cell.
[0011] From the above thing, a suitable specific surface area and the suitable mean particle diameter for the graphite powder for negative electrodes are importantly understood to be a bird clapper easily. It is indicated that invention proposed from such a viewpoint uses the graphite powder the specific surface area by the BET adsorption method is 1-10m2/g in JP,6-295725,A, and a mean particle diameter is 10-30 micrometers, and either [at least / whose] the content of powder with a particle size of 10 micrometers or less or the content of powder with a particle size of 30 micrometers or more is 10% or less. Furthermore, in JP,7-134988,A, the meso carbon micro bead which heat-treats and generates a petroleum pitch at low temperature is graphitized, the spacing (d002) of the field by the wide angle X-ray diffraction method (002) is 3.36-3.40A, and using the nodular-graphite powder whose specific surface area by the BET adsorption method is 0.7-5.0m2/g is indicated. Moreover, using the polyphase carbon matter with which specific surface area has 1/2 or less specific surface area of the nuclear carbon matter by below 20m2 / g in JP,5-307959,A is indicated.
[0012]
[Problem(s) to be Solved by the Invention] Invention mentioned above was effective for the reduction of

the irreversible capacity determined in early stages of a cycle which it is not only very effective for improvement in the high charge-and-discharge property of a rechargeable lithium-ion battery, and the electric discharge property at the time of low temperature, but can say that it is fatal. However, to the shelf life and reliability by neglect under an elevated temperature, it is inadequate and the dissatisfaction remained also in respect of the amount (mAh/g) of specific volume of a negative electrode, and capacity density (mAh/cc). this invention sets it as the purpose to aim at the further reliability of a lithium secondary battery, and an improvement of the formation of high-energy density.
[0013]
[Means for Solving the Problem] In order to solve the technical problem in the rechargeable lithium-ion battery mentioned above, this invention (1) Are based on a wide angle X-ray diffraction method. The spacing of a field (002) (d002) by less than 3.37A And the size of the microcrystal of C shaft orientations (Lc) At least 1000A or more (2) to an Ar-ion-laser Raman spectrum The R value which is the peak intensity ratio of 1360cm-1 to the peak intensity of 1580cm-1 which can be set is 0.3 or less. the thickness of the portion with the thinnest 1580cm-1 full width at half maximum whose or less [24cm -] 1 (3) mean particle diameter is 10-30 micrometers Below at least 3-micrometer or more mean particle diameter (4) The X diffraction peak intensity ratio of/(004) according [10.0m2 / below g(5) tapping density] in the specific surface area by the BET adsorption method to 0.5g/cc or more 1.0g[/cc] or less(6) wide-angle X-ray diffraction method (110) more than 3.5m2 / g 0.015 or more properties By using the shown massive graphite powder as a nucleus, calcinating by the 700-2800-degree C temperature requirement under inert gas atmosphere after covering a carbon precursor on the front face of the nucleus, and using the carbonaceous powder of the double layer structure in which the surface of a carbonaceous object was made to form as a negative-electrode material While making small irreversible capacity accepted in an initial cycle as much as possible, the shelf life and reliability of a cell in the neglect under an elevated temperature are improved, the outstanding high-rate-discharge property and the electric discharge property in low temperature are secured, and realization of a nonaqueous electrolyte rechargeable battery with the high amount of specific volume is enabled.
[0014]
[Embodiments of the Invention] Invention of this invention according to claim 1 is equipped with the separator allotted between a positive electrode, a negative electrode, and these. the aforementioned negative electrode As a negative-electrode material into which a lithium ion can repeat an intercalation and a day intercalation in reversible by charge and electric discharge (1) Are based on a wide angle X-ray diffraction method. The spacing of a field (002) (d002) by less than 3.37A And the size of the microcrystal of C shaft orientations (Lc) At least 1000A or more (2) to an Ar-ion-laser Raman spectrum The R value which is the peak intensity ratio of 1360cm-1 to the peak intensity of 1580cm-1 which can be set is 0.3 or less. the thickness of the portion with the thinnest 1580cm-1 full width at half maximum whose or less [24cm -] 1 (3) mean particle diameter is 10-30 micrometers Below at least 3-micrometer or more mean particle diameter (4) The X diffraction peak intensity ratio of/(004) according [10.0m2 / below g(5) tapping density] in the specific surface area by the BET adsorption method to 0.5g/cc or more 1.0g[/cc] or less(6) wide-angle X-ray diffraction method (110) more than 3.5m2 / g 0.015 or more properties The shown massive graphite powder is used as a nucleus. After covering a carbon precursor on the front face of the nucleus, While improving many properties of a rechargeable lithium-ion battery by calcinating by the 700-2800-degree C temperature requirement under inert gas atmosphere, and making it the nonaqueous electrolyte rechargeable battery using the carbonaceous powder of the double layer structure in which the surface of a carbonaceous object was made to form, high-energy density-ization can be attained.
[0015] The above (1) The massive graphite particle which has the property of - (6) is a high grade, and the natural or artificial shape of a scale and scale-like graphite of high crystallinity Chamfering-trituration and ****-trituration, By collecting what has the large thickness of a graphite powder, i.e., what is close to a globular form also in a scale-like particle, in process of sieving after balling-up trituration, specific surface area is not increased to ** and others, and tapping density can obtain 0.5 or more particles. Moreover, that the X diffraction peak intensity ratio of/(004) by the wide angle X-ray

diffraction method (110) at this time indicates 0.015 or more to be is good. Furthermore, it is the degree of mean-circle form (the boundary length of a granular-structure product equivalent circle is used as a molecule, and the boundary length of the picturized particle projection image by the ratio made into the denominator). it is set to 1, so that a particle image is close to a perfect circle, and a particle image is long and slender -- it is -- it is -- such a small value that it is carrying out convexo-concave one -- becoming -- that which is spheroidizing as 0.940 or more and a configuration factor is good Although the method of carrying out chamfering and sifting out after grinding to the shape of a disk and a tablet-like particle is raised, if it is process in which a scale-like graphite particle is further pulverized with a fluid energy grinder as an example and is the graphite particle which shows the physical properties of above-mentioned (1) - (6), especially the creation method will not be limited.

[0016] Although used suitably [10-30 micrometers of mean particle diameters of the above-mentioned graphite powder], 12-26 micrometers is more desirable, and 15-23 micrometers is the most desirable. At this time, when content of the powder which exceeds 10% or less or the particle size of 25 micrometers for the content of powder with a particle size of less than 10 micrometers preferably 20% or less is preferably made into 10% 20% or less, it is still more desirable. Furthermore, respectively, when the content of the powder exceeding the particle size of less than 10 micrometers and the particle size of 25 micrometers reaches 10% or less preferably and considers as 10% or less preferably 20% or less, respectively, it is the most desirable 20% or less. Although the specific surface area by the BET adsorption method can use the thing of the range of 3.5-10.0m2 / g, its 4.0-8.0m2 / g are desirable, and its 4.0-7.0m2 / g are the most desirable.

[0017] The graphite particles which carried out in this way and were selected although the theoretical values of the capacity per 1g of carbon on the basis of C6 Li of the intercalation compound which the intercalation of the lithium ion is carried out and it generates were 372mAh(s) are a charge-and-discharge rate 0.2 mA/cm2 Electric capacity measurement by the half cell using the lithium metal counter electrode carried out is performed, and if the amount of specific volume is more preferably close to 350 or more mAh/g and the above-mentioned geometric capacity, it will be suitably used by 330 or more mAh/g of nearer things.

[0018] As a carbon precursor for covering the graphite particle nucleus front face which can be used by this invention, first as the organic substance which advances carbonization by the liquid phase Coal system heavy oil, such as a coal tar pitch from a soft pitch to a hard pitch, and a coal liquid, Petroleum system heavy oil, such as naphtha tar division-into-equal-parts solution system heavy oil which carries out a byproduction at the time of pyrolysis of direct-current system heavy oil, such as an asphaltene, a crude oil, naphtha, etc., Heat treatment pitches, such as an ethylene tar pitch obtained by heat-treating decomposition system heavy oil, FCC decantation oil, and the Ashland pitch, etc. can be used. Furthermore, it is vinyl system macromolecules, such as a polyvinyl chloride, a polyvinyl acetate, a polyvinyl butyral, and polyvinyl alcohol, and 3. - 3 A methyl phenol formaldehyde resin, 5 - Matter, such as sulfur ring compounds, such as nitrogen ring compounds, such as aromatic hydrocarbons, such as substitution phenol resin, such as a dimethylphenol formaldehyde resin, an acenaphthylene, a deca cyclene, and an anthracene, a phenazine, and an acridine, and a thiophene, is raised. Moreover, a thermosetting resin raw material like thermosetting resin, such as aromatic system polymer, such as chain-like vinyl resin, such as naturally-ocurring polymers, such as a cellulose, a polyvinylidene chloride, and a polyacrylonitrile, and a polyphenylene, a furfuryl alcohol resin, phenol-formaldehyde resin, and an imido resin, or furfuryl alcohol as the organic substance which advances carbonization etc. is raised with solid phase. Suitably, by choosing a solvent and carrying out dissolution dilution, these organic substance is made to adhere to the front face of a graphite particle nucleus, and can be used if needed.

[0019] Although the carbonaceous powder of the double layer structure which made the surface of a carbonaceous object form in the front face of a graphite particle nucleus finally by usually heating what mixed this graphite particle nucleus and carbon precursor in the invention in this application, obtaining an intermediate product, carbonization-calcinating and grinding after that is obtained The rate of the carbonaceous object in the carbonaceous powder of a double layer structure is adjusted so that it may

become [50 or less % of the weight] 2 % of the weight or more 10 or less % of the weight preferably especially 1% of the weight or more 15 or less % of the weight still more preferably 0.5% of the weight or more 25 or less % of the weight 0.1% of the weight or more.
[0020] The manufacturing process for on the other hand obtaining the double layer carbonaceous object which the invention in this application requires is divided into the following four processes.
[0021] The 1st process graphite particle, a carbon precursor, the process that is further mixed using a mixer, a kneading machine, etc. of various marketing of a solvent if needed, and obtains mixture.
[0022] The process which obtains the intermediate product which heated stirring the aforementioned mixture if needed [2nd process], and removed the solvent.
[0023] The process which heats the 3rd process aforementioned mixture or an intermediate product at 700 degrees C or more 2800 degrees C or less under inert gas atmosphere, such as nitrogen gas, carbon dioxide gas, and argon gas, and obtains the carbonization matter.
[0024] The process which carries out [processing / classification / trituration, a crack,] fine-particles processing of the 4th process aforementioned carbonization matter if needed.
[0025] These the in-process 2nd process and, and the 4th process can be skipped depending on the case, and the 4th process may be performed before the 3rd process.
[0026] Moreover, as heat-treatment conditions for the 3rd process, heat history temperature conditions are important. Although the temperature minimum changes a little also with the kind of carbon precursor, and its heat histories, it is usually 900 degrees C or more preferably 700 degrees C or more. On the other hand, upper limit temperature can be raised to the temperature which does not have the structure order exceeding the crystal structure of a graphite particle nucleus fundamentally. Therefore, as upper limit temperature of heat treatment, 2800 degrees C or less are usually 2000 degrees C or less and a range with 1500 degrees C or less it is still more desirable and desirable preferably. In such heat treatment conditions, a programming rate, a cooling rate, heat treatment time, etc. can be arbitrarily set up according to the purpose. Moreover, after heat-treating in a low-temperature field comparatively, a temperature up can also be carried out to predetermined temperature. In addition, one set or two or more sets are sufficient as the reaction machine used for this process also at a batch process or continuous system again.
[0027] Thus, the carbonaceous powder material of the double layer structure of the invention in this application in which the surface of a carbonaceous object was made to form It is beyond the nuclear value not to exceed the degree of crystallinity of the graphite material used as a nucleus in the peak intensity ratio R value by Raman spectrum analysis and the value of d002 and Lc which are obtained in the diffraction diagram of X-ray wide angle diffraction, i.e., an R value. d002 value of half-value-width deltav is beyond the nuclear value beyond the nuclear value, and, as for Lc, it is desirable that it is below the nuclear value. As an R value of the carbonaceous powder material of a concrete double layer structure, it is mentioned preferably 1.0 or less [0.01 or more] that it is or more 0.2 0.4 or less range still more preferably, and is [or more 0.05] beyond a nuclear value 0.6 or less [0.1 or more] more preferably 0.8 or less. Moreover, although that whose mean particle diameter is 11-40 micrometers is used suitably, 13-30 micrometers is more desirable, and 16-25 micrometers is the most desirable. At this time, when content of the powder which exceeds 10% or less or the particle size of 25 micrometers for the content of powder with a particle size of less than 10 micrometers preferably 20% or less is preferably made into 10% or less 20% or less, it is still more desirable. Furthermore, respectively, when the content of the powder exceeding the particle size of less than 10 micrometers and the particle size of 25 micrometers reaches 10% or less preferably and considers as 10% or less preferably 20% or less, respectively, it is the most desirable 20% or less. Moreover, that whose average of the thickness of the thinnest portion of a particle is below 4-micrometer or more mean particle diameter is desirable. furthermore, the specific surface area by the BET adsorption method -- 1.0-5.0m2 / g -- more -- desirable -- 1.5-4.0m2 / g -- the thing of 2.0-3.5m2 / g is used suitably still more preferably Although the tapping density of the carbonaceous powder material of a double layer structure improves further rather than the nucleus graphite material used by carbon covering, it is desirable to control in the range of 0.7-1.2g/cc. The carbonaceous powder included in such a range is mixed with a binder or various additives,

and it fabricates so that it can be used as an electrode by methods, such as an application and sticking by pressure, on charge collectors, such as copper and nickel. The density (it is called plate density below) of the active material layer on an electrode is adjusted by rolling out by the monotonous press, the roll press, etc. after it. The capacity per unit volume of a cell can be pulled out to the maximum, without reducing the cell capacity at the time of low-temperature electric discharge of a cell, and a high rate discharge by carrying out to 1.5 or less [1.3 or more] more preferably by making plate density or less into 1.6 more greatly than 1.2 at this time. Thus, the cell constituted combining the created negative electrode and the metal chalcogenide type positive electrode for lithium ion batteries usually used can realize the 4V class high voltage, and its capacity is large, the irreversible capacity accepted in an initial cycle is small, the shelf life and reliability of a cell in the neglect under an elevated temperature are high, and it excels in a high-rate-discharge property and the electric discharge property in low temperature extremely. LixMO2 (M is one or more sorts of transition metals and x= 0 to 1.2) is suitable, and the chalcogenide type positive electrode in this case is LixCoO2, LixNiO2, and LixMn 2O4 especially. And what replaced a part of those Co(es), nickel, and Mn by elements, such as other transition metals, is suitable.

[0028] Although especially this invention does not limit the electrolytic solution, it is suitable to make into a principal component a chain-like carbonate [, such as one or more sorts of annular carbonate, such as the ethylene carbonate and propylene carbonate which are excellent in oxidation resistance and a low-temperature property as a solvent of the electrolytic solution used for the cell using the above-mentioned 4 Class V positive electrode and the negative electrode of this invention, and butylene carbonate, dimethyl carbonate and diethyl carbonate, and ethyl methyl carbonate, / one or more sorts of] mixed solvent. Moreover, other solvents, such as an aliphatic carboxylate and ether, are mixable if needed. a mixing ratio -- a rate -- volume conversion -- annular carbonate -- the solvent whole -- 20 - 80% of range has desirable chain-like carbonate 10 to 90% 15 to 40% especially 5 to 50% especially

[0029] Moreover, when using [class / 3V] the material of low voltage for a positive electrode comparatively, solvents other than the above-mentioned solvent can also be used.

[0030] Lithium salt is used for the solute of these solvents. the lithium salt generally known -- LiClO4, LiBF4, LiPF6, LiAlCl4, LiSbF6, LiSCN, LiCl, LiCF3 SO3, LiCF3 CO2, Li (CF3 SO2)2, LiAsF6, and LiN (CF3 SO2)2 etc. -- it is

[0031] About selection of a required member, restrictions are not prepared at all on cell composition other than the above.

[0032] The cell using the carbonaceous powder material of the double layer structure in which the surface of the above-mentioned carbonaceous object was made to form as a negative electrode improves high charge/discharge capability ability and the high-rate-discharge performance in low temperature compared with the cell using the carbonaceous powder material of the double layer structure in which the surface of a carbonaceous object was made to form using the graphite particle which does not have the graphite particle or the property of above-mentioned (1) - (6) of not making the surface of a carbonaceous object forming as a negative electrode. Moreover, it is hard to make the organic solvent in the electrolytic solution decompose also under an elevated temperature, and since it becomes that it is hard to carry out elevation of cell internal pressure, the liquid spill accident of the electrolytic solution which was a problem conventionally can be prevented. Moreover, since specific surface area becomes small by making it the carbonaceous powder of a double layer structure, also under an elevated temperature, it is hard to make the organic solvent in the electrolytic solution decompose, and degradation of the cell performance in an elevated temperature can be made small.

[0033]

[Example] Hereafter, the operation gestalt of this invention is explained in detail using a chart.

[0034] (Measuring method)

(1) About one cc of 2vol% solution of polyoxyethylene (20) sorbitan monolaurate was used for the volume criteria mean-particle-diameter surfactant, this was beforehand mixed to carbonaceous powder, and the volume criteria mean particle diameter (median size) was measured by making ion exchange water into a dispersion medium after an appropriate time with the laser diffraction formula particle-size-

distribution plan "LA-700" by Horiba, Ltd.
[0035] (2) After using the screen of 300 micrometers of openings, dropping fine particles in the 20 cc tapping cell and filling up with a cell to the limit, to the screen which a sample penetrates using a tapping density Seishin Enterprise milling volume density measuring instrument "tap DIN sir KYT-3000", tapping which is 10mm of stroke length was performed 1000 times, and the tapping density at that time was measured to it.
[0036] (3) After heating at 350 degrees C as predrying and pouring nitrogen gas for 15 minutes using 8000, it measured by the one AMS[by BET specific surface area measurement Ohkurariken CO., LTD.]-BET method in the phase counter pressure 0.3 by nitrogen gas adsorption.
[0037] (4) To the X diffraction sample, about 15% of X-ray standard high-purity-silicon powder was added, it mixed, the sample cell was stuffed, the CuK alpha rays monochrome-ized with the graphite monochromator were made into the line source, and the wide angle X diffraction curve was measured by the reflective formula differential-gear RAKUTO meter method. Based on the **** method, the size (Lc) of the microcrystal of the spacing (d002) of a field (002) and C shaft orientations was measured for the wide angle X diffraction curve obtained by measurement.
[0038] (5) the Raman assay-date book -- a spectrum -- shrine make -- the Raman spectrum analysis using Ar-ion-laser light with a wavelength of 514.5nm using NR-1800 -- setting -- the intensity IA of the peak PA of a near [1580cm-1], and the intensity IB of the peak PB of the range of 1360cm-1 -- measuring -- the ratio of the intensity -- R=IB/IA was measured Moreover, the half-value width of the peak PA of a near [1580cm-1] was asked for the wave number (cm-1) as a unit. It measured by rotating a cell in a field perpendicular to a laser beam, having filled up the cell with the thing of a powder state by natural fall, and irradiating a laser beam on the sample front face in a cell in manufacture of a sample.

[0039] (6) The average of the thickness in the average carbon-powder end of the thickness of the thinnest portion in the end of a carbon powder searched for the molding object from the SEM image of the pressurization direction and the field cut to parallel, after carrying out pressing of each sample offering graphite powder using metal mold. That is, 100 or more values of the thickness direction of the thinnest portion in the end of a carbon powder were measured, and the average was calculated.
[0040] (7) Using metal mold, the X-ray peak intensity ratio of measurement (110)/(004) of the X-ray peak intensity ratio of (110)/(004) pressurized the end of a carbon powder, fabricated it with a density of about 1.7 g/cc in the shape of a pellet, computed the peak intensity ratio of/(004) obtained by wide angle X diffraction measurement (110), and calculated the average. (004) The diffraction line of a field and a field (110) is a diffraction line in the carbon six membered ring reticulated flat surface of a graphite crystal, and its vertical plane. When there are many scale configurations, compared with the case where there are many graphite particles of the shape of the shape of a disk and a tablet, a graphite particle carries out orientation to a pressurization side and a parallel direction alternatively at the time of pellet creation. Therefore, if a scale-like particle increases compared with the graphite particle of the shape of the shape of a disk, and a tablet (110), a /(004) peak intensity ratio will become small.
[0041] (8) The flow formula particle image analysis apparatus "FPIA-1000" by measurement TOA Medical Electronics Co., Ltd. of the degree of mean-circle form was used, the graphite particle distributed in water was picturized every [1/] 30 seconds by the CCD camera, and the degree of mean-circle form to all particles was computed by carrying out real-time analysis of the particle image. Ion exchange water was used for the dispersion medium, and polyoxyethylene (20) sorbitan monolaurate was used for the surfactant. the degree of mean-circle form is the ratio which used the boundary length of a particle projected-area equivalent circle as the molecule, and made the denominator the boundary length of the picturized particle projection image, it is set to 1, so that a particle image is close to a perfect circle, and a particle image is long and slender -- it is -- it is -- it becomes such a small value that it is carrying out convexo-concave one
[0042] (Example 1 of a fundamental experiment) Drawing 1 is the cross section of the coin form cell for measuring the reversible capacitance and irreversible capacity of a negative electrode of a rechargeable lithium-ion battery. In drawing 1 , spot welding of the grid 3 which becomes the inner base of the cell

case 1 made from stainless steel from the expanded metal made from stainless steel is carried out beforehand, and the mixture which makes a principal component the carbon-powder end for negative electrodes of this grid 3 and a rechargeable lithium-ion battery is fixed to one as a carbon electrode 5 by the casting-in can method. The mixture of a carbon electrode 5 mixes the end for a sample offering of a carbon powder, and an acrylic binder by the ratio of 100:5 by the weight ratio. The gasket 7 made from polypropylene is attached in the periphery of the cover 2 made from stainless steel, and the metal lithium 4 is stuck to the inside of a cover 2 by pressure. After making a carbon electrode 5 carry out **** sinking in of the nonaqueous electrolyte, distributor shaft coupling of the cover 2 with gasket 7 is carried out to the cell case 1 through the separator 6 which consists of a microporosity polyethylene film, inboard is made to curl and upper-limb opening of the cell case 1 is obturated. In addition, as nonaqueous electrolyte, the organic electrolytic solution which made the concentration of 1 mol/l dissolve a 6 fluoride [phosphoric-acid] lithium in the mixed solvent of the volume ratio 1:1 of ethylene carbonate and diethyl carbonate was used. It is current density 0.3 mA/cm2 at a 20-degree C basis, using the sample offering carbon-powder end of 14 kinds for a carbon electrode 5, producing a cell, and using a positive electrode and the metal lithium electrode 4 as a negative electrode for a carbon electrode 5. It charges and discharges by the constant current. Let the amount which deintercalated and asked for the lithium from carbon be a reversible capacitance until cell voltage is set to 1.0V, after intercalating a lithium in carbon until cell voltage is set to 0V. The value which **(ed) the reversible capacitance from quantity of electricity which intercalation took was made into irreversible capacity. In addition, the charge-and-discharge final-voltage value of these test cells is negative-electrode carbon / positive electrode LiCoO2. It is mostly equivalent to charge final-voltage 4.20V of the practical use cell of a system, and discharge-final-voltage 2.75V.

[0043] tapping density was raised by the scale-like artificial graphite, the natural graphite, and the various trituration methods which grind by the conventional method and are acquired -- as artificial, natural-graphite powder (sample No.1-15), and a comparison sample with them The spherical meso carbon micro bead which graphitized the meso carbon micro bead currently indicated by JP,7-134988,A (it MCMB(s)) Sample No.16 and petroleum-pitch-coke powder (sample No.17) are made into the end for negative electrodes of a sample offering carbon powder, and the physical-properties value of these powder, the reversible capacitance mentioned above, and irreversible capacity are collectively shown in Table 1.

[0044]

[Table 1]

試料No.	原材料	製造元	商品名	粉末物性値 d002 (Å)	Lc (Å)	ラマンR値	ラマン半値幅 (cm⁻¹)	平均粒径 (μm)	比表面積 (m²/g)	最薄部平均厚さ (μm)	タッピング密度 (g/cc)	平均円形度	(110)/(004)	電気特性 可逆容量 (mAh/g)	不可逆容量 (mAh/g)
1	人造黒鉛	ティムカル	KS15	3.36	1000以上	0.16	21.1	7.8	14.5	1.1	0.32	0.928	0.008	351	53
2	人造黒鉛	ティムカル	KS25	3.36	1000以上	0.16	21.4	10.1	11.9	1.3	0.40	0.925	0.009	353	43
3	人造黒鉛	ティムカル	KS44	3.36	1000以上	0.15	22.2	18.8	9.3	1.8	0.41	0.919	0.010	359	36
4	人造黒鉛	ティムカル	KS75	3.36	1000以上	0.15	22.2	23.7	7.2	2.1	0.44	0.918	0.011	353	35
5	人造黒鉛	日本黒鉛	SP-10	3.35	1000以上	0.18	21.2	32.5	6.9	2.4	0.41	0.927	0.012	353	32
6	人造黒鉛	日本黒鉛	SP-20	3.36	1000以上	0.15	24.0	14.9	8.7	1.8	0.23	0.937	0.010	356	40
7	天然黒鉛	エスイーシー	SNO10	3.35	1000以上	0.19	20.9	10.4	8.7	2.0	0.46	0.919	0.008	362	39
8	天然黒鉛	エスイーシー	SNO15	3.35	1000以上	0.17	21.5	12.9	7.8	2.3	0.46	0.927	0.009	361	35
9	天然黒鉛	エスイーシー	SNO20	3.36	1000以上	0.16	21.6	18.7	6.8	2.5	0.48	0.930	0.009	358	34
10	天然黒鉛	日本黒鉛	ACP-20NB	3.36	1000以上	0.18	21.6	19.0	4.9	5.4	0.64	0.947	0.038	354	23
11	天然黒鉛	日本黒鉛	ASP-20NB	3.36	1000以上	0.17	21.1	16.7	4.9	6.3	0.66	0.943	0.039	357	20
12	人造黒鉛	日本黒鉛	SP-20NB	3.36	1000以上	0.20	20.9	15.7	6.6	3.5	0.61	0.942	0.032	360	26
13	天然黒鉛	中越黒鉛	H-0	3.36	1000以上	0.21	22.0	22.3	5.6	5.6	0.65	0.940	0.035	358	24
14	天然黒鉛	中越黒鉛	H-1	3.36	1000以上	0.18	21.8	18.4	5.8	6.5	0.79	0.941	0.038	355	24
15	天然黒鉛	中越黒鉛	H-2	3.36	1000以上	0.24	22.1	17.7	6.4	5.8	0.70	0.940	0.039	356	26
16	人造黒鉛	大阪ガス	MCMB	3.37	700	0.19	25.4	5.3	2.9	5.3	1.10	0.966	0.120	295	18
17	人造黒鉛	日本黒鉛	GMW-20NB	3.37	750	0.32	25.0	17.2	5.3	8.1	0.95	0.961	0.110	298	27

[0045] The nodular-graphite powder (sample No.16) and corks powder (sample No.17) of a comparison sample of both reversible capacitances which influence an energy density greatly the result of Table 1 to whose Lc is less than 1000A were as small as less than 300 mAh/g, although irreversible capacity was comparatively small. To these, raw material is 350 mAh/g at least, and all of the reversible capacitance of sample No.1-15 of a natural graphite and artificial-graphite powder became the value approximated to the theoretical value (372 mAh/g) of the amount of specific volume. In these, the irreversible capacity of the graphite powder of sample No.10-15 is 20 - 26 mAh/g, and it attracts attention that it is smaller than that of other graphite powders (sample No.1-9).

[0046] It is understood that a reversible capacitance higher level than using for the negative-electrode material of a rechargeable lithium-ion battery a natural graphite or an artificial graphite with high degree of crystallinity and purity whose size (Lc) of the microcrystal of C shaft orientations the spacing (d002) of the field by the wide angle X diffraction (002) is less than 3.37A as a prerequisite of this invention, and is at least 1000A or more is obtained.
[0047] (Example 2 of a fundamental experiment) In the example 1 of a fundamental experiment, using the end for negative electrodes of a carbon powder (sample No.1-17) a reversible capacitance and irreversible capacity were calculated, the cylindrical shape cell was produced and the liquid spill nature at the time of carrying out elevated-temperature neglect in the state of the high-rate-discharge property in low temperature and charge was measured.
[0048] Drawing 2 is the cross section of the cylindrical shape cell of spiral electrode group composition. In drawing 2 , the band-like positive electrode 10 of one sheet each and a negative electrode 11 are spirally wound through the separator 12 which consists of a microporosity polyethylene film, and an electrode group is constituted. A positive electrode 10 is LiCoO2 which is the multiple oxide of the lithium of active material material, and cobalt. The after [dryness] roll press of the paste mixed at a rate of 100:3:10 is applied and carried out to both sides of the aluminum foil which is a charge collector by the weight ratio, and the carbon black of electric conduction material and the polytetrafluoroethylene (PTFE) of a binder are judged in a predetermined size. In addition, PTFE of a binder used the thing of a dispersion solution. Spot welding of the piece 13 of a positive-electrode lead is carried out to the aluminum foil of a positive electrode 10. A negative electrode 11 applies and carries out the after [dryness] roll press of the paste which added the acrylic binder solution in the end of a sample offering carbon powder, and was mixed to both sides of the copper foil which is a charge collector, and cuts it out in a predetermined size. Spot welding of the piece 14 of a negative-electrode lead is carried out to the copper foil of a negative electrode 11. After equipping the inferior surface of tongue of the wound electrode group with the pars-basilaris-ossis-occipitalis electric insulating plate 15 and holding in the cell case 16 made from nickel ******, spot welding of the piece 14 of a negative-electrode lead is carried out to the inner base of the cell case 16. After laying the up electric insulating plate 17 on an electrode group after that, grooving is carried out to the predetermined position of opening of the cell case 16, and it carries out pouring sinking in of the organic electrolytic solution of the specified quantity. The organic electrolytic solution same as the organic electrolytic solution as the example 1 of a fundamental experiment was used. Then, spot welding of the piece 13 of a positive-electrode lead is carried out to the inner base of the obturation board 19 with which the gasket 18 was attached in the periphery. The obturation board 19 is inserted in opening of the cell case 16 through a gasket 18, and a cell will be completed if the upper limb of the cell case 16 is curled and obturated to inboard.
[0049] The service capacity of each cell was regulated by negative-electrode capacity, and made the same carbon-powder Shigekazu Sue of each cell for negative electrodes irrespective of the kind. The amount of other part material used and the production method are completely made the same, and could be made to perform comparison in the end for negative electrodes of a carbon powder.
[0050] About cell A-Q five cells each using the carbon-powder end for negative electrodes of 17 kinds, after charging all the cells at 20 degrees C until the terminal voltage of each cell became 4.2V at 100mA (1/5C) constant current, it discharged to 2.75V by 100mA (1/5C) constant current, and 1 / 5C service capacity was calculated. Then, after charging similarly, it discharged to 2.75V by 500mA (1C) constant current, and 1C service capacity was calculated. Subsequently, after charging at 20 degrees C, it was left at -20 degrees C for 24 hours, and 1C service capacity was calculated at the same -20 degrees C. After putting each cell on 20 degrees C gently, restoring the temperature of a cell to 20 degrees C, and charging by the same cell, and it left it at 100 degrees C on the 1st and the temperature of a cell became 20 degrees C, the existence of a liquid spill was observed about all cells.
[0051] As contrasted with the physical-properties value in the end of a sample offering carbon powder, the cell performance (average of five cells) mentioned above is summarized, and it is shown in Table 2.
[0052]
[Table 2]

試料 No.	原材料	製造元	商品名	セル記号	電池性能			
					1/5C 放電容量	1C 放電容量	-20℃1C 放電容量	高温放置後 漏液数
1	人造黒鉛	ティムカル	KS15	A	511	501	450	5/5
2	人造黒鉛	ティムカル	KS25	B	532	523	452	3/5
3	人造黒鉛	ティムカル	KS44	C	539	521	410	2/5
4	人造黒鉛	ティムカル	KS75	D	549	508	357	0/5
5	人造黒鉛	日本黒鉛	SP-10	E	537	483	267	1/5
6	人造黒鉛	日本黒鉛	SP-20	F	541	528	433	2/5
7	天然黒鉛	エスイーシー	SNO10	G	538	522	473	3/5
8	天然黒鉛	エスイーシー	SNO15	H	545	531	452	2/5
9	天然黒鉛	エスイーシー	SNO20	I	536	520	407	1/5
10	天然黒鉛	日本黒鉛	ACP-20NB	J	554	543	421	0/5
11	天然黒鉛	日本黒鉛	ASP-20NB	K	561	550	445	0/5
12	人造黒鉛	日本黒鉛	SP-20NB	L	557	546	440	0/5
13	天然黒鉛	中越黒鉛	H-0	M	553	541	420	0/5
14	天然黒鉛	中越黒鉛	H-1	N	554	545	440	0/5
15	天然黒鉛	中越黒鉛	H-2	O	560	548	445	0/5
16	人造黒鉛	大阪ガス	MCMB	P	478	463	417	0/5
17	人造黒鉛	日本黒鉛	GMW-20NB	Q	483	468	372	0/5

[0053] sample No. whose reversible capacitance shown from Table 2 in Table 1 was small -- although 20-degree C 1/5C and 1C service capacity of 16 and 17 are low, they of the graphite powder of sample No.1-15 are relatively large That however, the high-rate-discharge capacity (-20 degrees C, 1C) in low temperature showed 400mA or more among sample No.1-15 They were sample No.1 and the cells A, B, C, F, G, H, I, J, K, L, M, N, and O by the graphite powder of 2, 3, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15. Furthermore, it was the cells D, J, K, L, M, N, O, P, and Q by sample No.4 and the carbon-powder end of 10, 11, 12, 13, 14, 15, 16, and 17 that a liquid spill was not accepted at all after elevated-temperature neglect. Ranging from these results to all cell performances, sample No.10 and the cells J, K, L, M, N,

and O by the graphite powder of 11, 12, 13, 14, and 15 were excellent.
[0054] (An example and example of comparison) In the cell which measured the liquid spill nature at the time of leaving it in the example 2 of a fundamental experiment under 1 / 5C service capacity, 1C service capacity, -20-degree C 1C service capacity, and an elevated temperature The cell J by the graphite powder of sample No.10, and 11, 12, 13, 14 and 15 which was excellent covering all cell properties After leaving the cell of K, L, M, N, and O under an elevated temperature, when 20-degree C 1 / 5C service capacity were calculated on the charge-and-discharge conditions indicated for the example 2 of a fundamental experiment, compared with 1 / 5C service capacity before leaving it under an elevated temperature, only 70 - 80% of service capacity was shown. Although the reliability of a cell improved, degradation of a cell property is intense, and when left under an elevated temperature, it is necessary for the liquid spill accident by the neglect under an elevated temperature to have none of these cells, and to make degradation of a cell property small.
[0055] Then, by using as a nucleus the end for negative electrodes of a carbon powder (sample No.1-17) the cell performance was measured in the example 2 of a fundamental experiment, finally it heat-treated at 1200 degrees C under the inert gas style after covering, respectively, so that it might become 5% of the weight after carbonization, using the petroleum system tar pitch obtained at the time of naphtha cracking as a carbon precursor. Then, it cracked after cooling using the grinder to the room temperature, and the end of a carbon system composite powder with the fixed particle size distribution was obtained. In this way, the carbonaceous powder (sample No.18-34) of the double layer structure which made the surface of a new carbonaceous object form on a nuclear front face was created, and it considered as the end for negative electrodes of a sample offering carbon powder.
[0056] having produced each five cell of cell R-AH like the example 2 of a fundamental experiment, respectively, and having measured the same cell performance except having used the carbon-powder end for negative electrodes of 17 kinds, -- in addition, 1 / 5C service capacity of a cell as which the liquid spill after elevated-temperature neglect was not regarded were measured
[0057] The cell performance mentioned above to the physical-properties value in the end of a sample offering carbon powder is collectively shown in Table 3.
[0058]
[Table 3]

試料No.	核材試料No.	原材料	製造元	商品名	粉末物性値 平均粒径 (µm)	比表面積 (m²/g)	最薄部平均厚さ (µm)	タッピング密度 (g/cc)	セル記号	電池性能 1/5C放電容量 (mAh)	1C放電容量 (mAh)	-20℃1C放電容量 (mAh)	高温放置後漏液数	高温放置後1/5C放電容量 (mAh)	高温放置前後の1/5C放電容量比 (%)
18	1	人造黒鉛	ティムカル	KS15	12.0	4.9	1.9	0.47	R	520	513	448	4/5	-	-
19	2	人造黒鉛	ティムカル	KS25	12.4	4.5	2.4	0.57	S	542	530	454	2/5	-	-
20	3	人造黒鉛	ティムカル	KS44	17.7	4.2	2.6	0.61	T	549	532	411	1/5	-	-
21	4	人造黒鉛	ティムカル	KS75	23.2	3.1	3.1	0.74	U	553	520	357	0/5	455	82.3
22	5	人造黒鉛	日本黒鉛	SP-10	38.8	2.5	3.3	0.62	V	547	490	269	1/5	-	-
23	6	人造黒鉛	日本黒鉛	SP-20	22.9	4.8	2.7	0.57	W	549	535	434	2/5	-	-
24	7	天然黒鉛	エスイーシー	SNO10	18.6	4.1	3.1	0.82	X	541	530	475	2/5	-	-
25	8	天然黒鉛	エスイーシー	SNO15	21.4	3.7	3.2	0.81	Y	554	537	452	1/5	-	-
26	9	天然黒鉛	エスイーシー	SNO20	25.2	2.9	3.4	0.83	Z	542	528	409	1/5	-	-
27	10	天然黒鉛	日本黒鉛	ACP-20NB	20.2	2.5	8.1	0.81	AA	566	552	423	0/5	531	93.8
28	11	天然黒鉛	日本黒鉛	ASP-20NB	21.4	2.8	10.2	0.88	AB	569	559	447	0/5	534	93.8
29	12	人造黒鉛	日本黒鉛	SP-20NB	21.5	2.8	4.9	0.70	AC	567	549	443	0/5	532	93.8
30	13	天然黒鉛	中越黒鉛	H-0	24.8	2.3	7.6	0.85	AD	560	550	425	0/5	530	94.6
31	14	天然黒鉛	中越黒鉛	H-1	24.0	2.4	10.5	0.94	AE	561	552	458	0/5	532	94.8
32	15	天然黒鉛	中越黒鉛	H-2	21.2	2.6	8.3	0.92	AF	563	557	462	0/5	537	95.4
33	16	人造黒鉛	大阪ガス	MCMB	6.5	1.8	6.1	1.26	AG	485	570	415	0/5	450	92.8
34	17	人造黒鉛	日本黒鉛	GMW-20NB	17.2	1.6	8.7	1.05	AH	487	473	374	0/5	452	92.8

[0059] From Table 3, change of 1 / 5C service capacity by making it the carbonaceous powder of a double layer structure, 1C service capacity, and -20-degree-C1C service capacity was not seen. However, the cell R by the carbonaceous powder sample (No.18, 19, 20, 22, 23, 24, 25, 26) of sample No.1 as which the liquid spill was regarded in the example 2 of a fundamental experiment, and the double layer structure which used 2, 3, 5, 6, 7, 8, and 9 as the nucleus Although the number of liquid spills of S, T, V, W, X, Y, and Z showed the inclination which decreases, it was inadequate for stopping a liquid spill. On the other hand, it was the cells U, AA, AB, AC, AD, AE, AF, AG, and AH by the carbonaceous powder of the double layer structure of samples 21, 27, 28, 29, 30, 31, 32, 33, and 34 that

a liquid spill was not accepted at all after elevated-temperature neglect. 1 / 5C service capacity after elevated-temperature neglect of these cells became 82 - 96% of value to 1 / 5C service capacity before elevated-temperature neglect, and 1 / 5C service capacity after elevated-temperature neglect improved by making it the carbonaceous powder of a double layer structure. In these, all 1 / 5C service capacity after elevated-temperature neglect are at least 530 or more mAhs, and the cells AA, AB, AC, AD, AE, and AF by the carbonaceous powder of the double layer structure of samples 27, 28, 29, 30, 31, and 32 became 93% or more of value to 1 / 5C service capacity before elevated-temperature neglect. Ranging from these results to all cell performances, the cells AA, AB, AC, AD, AE, and AF by the carbonaceous powder of sample No.27 and the double layer structure of 28, 29, 30, 31, and 32 were excellent.
[0060] In addition, although burning temperature was carried out at 1300 degrees C in order to obtain the carbonaceous powder of a double layer structure in the above, by the 700 degrees C - 2800 degrees C temperature requirement, the same powder physical properties were acquired and the same effect as this invention was seen. Moreover, although the carbonaceous powder of a double layer structure mixed and produced the charge of karyomitome, and the pitch so that the weight ratio of the graphite powder used for the nucleus and the carbon matter in which the surface was made to newly form might be set to 95:5, physical properties with these weight ratios same in 99:1-50:50 were acquired, and the same effect as this invention was acquired.
[0061] Moreover, in the above, although only the organic electrolytic solution was explained as nonaqueous electrolyte about this invention, it does not bar applying to the rechargeable battery which consists of cation conductivity solid electrolytes, such as polymer.
[0062]
[Effect of the Invention] By using the graphite powder for negative electrodes by this invention as mentioned above, it is at least 95% of 354 - 360 mAh/g (95.2 - 96.8%) of the theoretical value (372 mAh/g) of the amount of specific volume, and irreversible capacity is as small as 20 - 26 mAh/g, and is **(ed) to improvement in an energy density. Furthermore, high charge and discharge and a low-temperature high-rate-discharge performance are not only excellent, but liquid spill accident does not occur by elevated-temperature neglect, either, but it can do so the effect that degradation of a cell performance can also offer a reliable small lithium secondary battery.

[Translation done.]

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to a nonaqueous electrolyte rechargeable battery, especially relates to the carbon material for negative electrodes of a rechargeable lithium-ion battery.

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PRIOR ART

[Description of the Prior Art] Conventionally, as a nonaqueous electrolyte rechargeable battery, it aims at high-energy density-ization by the high voltage and high capacity, and the so-called lithium secondary battery using the organic electrolytic solution which consists of an organic-solvent solution of lithium salt as nonaqueous electrolyte, such as chalcogen compounds, for example, manganese dioxide, molybdenum disulfide, selenium-ized titanium, etc., such as the oxide and sulfide of transition metals, and a selenide, is examined as a metal lithium and a positive active material as a negative-electrode active material.

[0003] However, although this lithium secondary battery can choose the intercalation compound in which the charge-and-discharge property was comparatively excellent as a positive active material, the charge-and-discharge property of the metal lithium of a negative electrode is not necessarily excellent. Therefore, it was difficult to lengthen the cycle life which repeats charge and discharge, there was a possibility that generation of heat by the internal short circuit might moreover take place, and the problem was in safety. That is, the metal lithium of a negative-electrode active material is eluted as a lithium ion in the organic electrolytic solution by electric discharge. The eluted lithium ion has some which deposit as an activity shape [shape of arborescence or moss] metallic crystal by charge, without depositing flat and smooth altogether like origin although deposited on a negative-electrode front face as a metal lithium. The front face of the metallic crystal itself is being worn with a passive state coat, and is inactivated, and an activity metallic crystal stops being able to contribute it to electric discharge easily while decomposing the organic solvent in the electrolytic solution. Consequently, since negative-electrode capacity fell as the charge-and-discharge cycle progressed, negative-electrode capacity needed to be made remarkably larger than that of a positive electrode at the time of cell production. Moreover, an activity arborescence metal lithium crystal may penetrate separator, may contact a positive electrode, and may carry out an internal short circuit. By the internal short circuit, a cell has a possibility of generating heat.

[0004] Then, as a negative-electrode material, the so-called rechargeable lithium-ion battery using the carbon material which can repeat an intercalation and a day intercalation in reversible is proposed by charge and electric discharge, research and development is actively done, and the utilization stage is already greeted by them. Since an activity arborescence metal lithium crystal does not deposit on a negative-electrode front face at the time of charge and discharge unless this rechargeable lithium-ion battery is overcharged, improvement in safety can expect very much. Furthermore, since this cell excels remarkably the lithium secondary battery which uses a metal lithium for a negative-electrode active material in the high charge-and-discharge property and the cycle life, the need of this cell is elongated quickly in recent years.

[0005] LiCoO2 which is equivalent to an electric discharge state as a positive active material of a 4V class rechargeable lithium-ion battery, LiNiO2, LiMnO2, and LiMn 2O4 etc. -- the multiple oxide of a lithium and transition metals is adopted or examined As an electrolyte, nonaqueous electrolyte, such as the organic electrolytic solution and a polymer solid electrolyte, is used like a lithium secondary battery.

[0006] When a graphite is used for negative-electrode material, the theoretical values of the capacity per 1g of carbon on the basis of C6 Li of the intercalation compound which the intercalation of the lithium ion is carried out and it generates are 372mAh(s). Therefore, in various carbon material, you should choose that to which the theoretical value of this amount of specific volume is approached, and it becomes high as much as possible as a negative electrode of a practical use cell, the capacity value (mAh/cc), i.e., the capacity density, per unit volume.
[0007] In the difficulty graphitized carbon commonly called a hard carbon among various carbon material, the material exceeding said amount theoretical value of specific volume (372 mAh/g) is found out, and examination is advanced. However, the true specific gravity of the amorphous carbon of difficulty graphitization nature is small, and since it is bulky, it is substantially difficult [it] to enlarge capacity density of a negative electrode. It cannot be said as **, so that the negative-electrode potential after charge moreover resembles metal lithium potential, but a discharge potential has many technical problems, like flat nature is also inferior.
[0008] On the other hand, since the potential after charge is approximated to metal lithium potential, and the flat nature of a discharge potential is also excellent and a charge-and-discharge property improves as a practical use cell when a natural graphite with high crystallinity and artificial-graphite powder are used for a negative electrode, recently, graphite system powder is becoming in use [negative-electrode material].
[0009] It is in it, and if the mean particle diameter of the graphite powder for negative electrodes of a rechargeable lithium-ion battery is large, there is an inclination for the charge-and-discharge property in high rate and the electric discharge property in low temperature to be inferior.
[0010] Then, if a powdered mean particle diameter is made small and a mean particle diameter will be made small too much at ** and others although a high charge-and-discharge property and a low-temperature electric discharge property improve, when a powdered specific surface area becomes large too much, the problem to which the irreversible capacity which the lithium inserted by the initial charge into powder cannot contribute to the electric discharge after the 1st cycle becomes large will arise. While this phenomenon was a fatal fault, when a cell was left to a high-energy density-ized intention under an elevated temperature which exceeds 100 degrees C, it makes the solvent in the organic electrolytic solution disassemble, has a possibility of it not only carrying out self-discharge, but raising cell internal pressure and causing liquid spill accident, and had become the cause of reducing the reliability of a cell.
[0011] From the above thing, a suitable specific surface area and the suitable mean particle diameter for the graphite powder for negative electrodes are importantly understood to be a bird clapper easily. It is indicated that invention proposed from such a viewpoint uses the graphite powder the specific surface area by the BET adsorption method is 1-10m2/g in JP,6-295725,A, and a mean particle diameter is 10-30 micrometers, and either [at least / whose] the content of powder with a particle size of 10 micrometers or less or the content of powder with a particle size of 30 micrometers or more is 10% or less. Furthermore, in JP,7-134988,A, the meso carbon micro bead which heat-treats and generates a petroleum pitch at low temperature is graphitized, the spacing (d002) of the field by the wide angle X-ray diffraction method (002) is 3.36-3.40A, and using the nodular-graphite powder whose specific surface area by the BET adsorption method is 0.7-5.0m2/g is indicated. Moreover, using the polyphase carbon matter with which specific surface area has 1/2 or less specific surface area of the nuclear carbon matter by below 20m2 / g in JP,5-307959,A is indicated.

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EFFECT OF THE INVENTION

[Effect of the Invention] By using the graphite powder for negative electrodes by this invention as mentioned above, it is at least 95% of 354 - 360 mAh/g (95.2 - 96.8%) of the theoretical value (372 mAh/g) of the amount of specific volume, and irreversible capacity is as small as 20 - 26 mAh/g, and is **(ed) to improvement in an energy density. Furthermore, high charge and discharge and a low-temperature high-rate-discharge performance are not only excellent, but liquid spill accident does not occur by elevated-temperature neglect, either, but it can do so the effect that degradation of a cell performance can also offer a reliable small lithium secondary battery.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Invention mentioned above was effective for the reduction of the irreversible capacity determined in early stages of a cycle which it is not only very effective for improvement in the high charge-and-discharge property of a rechargeable lithium-ion battery, and the electric discharge property at the time of low temperature, but can say that it is fatal. However, to the shelf life and reliability by neglect under an elevated temperature, it is inadequate and the dissatisfaction remained also in respect of the amount (mAh/g) of specific volume of a negative electrode, and capacity density (mAh/cc). this invention sets it as the purpose to aim at the further reliability of a lithium secondary battery, and an improvement of the formation of high-energy density.

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MEANS

[Means for Solving the Problem] In order to solve the technical problem in the rechargeable lithium-ion battery mentioned above, this invention (1) Are based on a wide angle X-ray diffraction method. The spacing of a field (002) (d002) by less than 3.37A And the size of the microcrystal of C shaft orientations (Lc) At least 1000A or more (2) to an Ar-ion-laser Raman spectrum The R value which is the peak intensity ratio of 1360cm-1 to the peak intensity of 1580cm-1 which can be set is 0.3 or less. the thickness of the portion with the thinnest 1580cm-1 full width at half maximum whose or less [24cm -] 1 (3) mean particle diameter is 10-30 micrometers Below at least 3-micrometer or more mean particle diameter (4) The X diffraction peak intensity ratio of/(004) according [10.0m2 / below g(5) tapping density] in the specific surface area by the BET adsorption method to 0.5g/cc or more 1.0g[/cc] or less(6) wide-angle X-ray diffraction method (110) more than 3.5m2 / g 0.015 or more properties By using the shown massive graphite powder as a nucleus, calcinating by the 700-2800-degree C temperature requirement under inert gas atmosphere after covering a carbon precursor on the front face of the nucleus, and using the carbonaceous powder of the double layer structure in which the surface of a carbonaceous object was made to form as a negative-electrode material While making small irreversible capacity accepted in an initial cycle as much as possible, the shelf life and reliability of a cell in the neglect under an elevated temperature are improved, the outstanding high-rate-discharge property and the electric discharge property in low temperature are secured, and realization of a nonaqueous electrolyte rechargeable battery with the high amount of specific volume is enabled.
[0014]
[Embodiments of the Invention] Invention of this invention according to claim 1 is equipped with the separator allotted between a positive electrode, a negative electrode, and these. the aforementioned negative electrode As a negative-electrode material into which a lithium ion can repeat an intercalation and a day intercalation in reversible by charge and electric discharge (1) Are based on a wide angle X-ray diffraction method. The spacing of a field (002) (d002) by less than 3.37A And the size of the microcrystal of C shaft orientations (Lc) At least 1000A or more (2) to an Ar-ion-laser Raman spectrum The R value which is the peak intensity ratio of 1360cm-1 to the peak intensity of 1580cm-1 which can be set is 0.3 or less. the thickness of the portion with the thinnest 1580cm-1 full width at half maximum whose or less [24cm -] 1 (3) mean particle diameter is 10-30 micrometers Below at least 3-micrometer or more mean particle diameter (4) The X diffraction peak intensity ratio of/(004) according [10.0m2 / below g(5) tapping density] in the specific surface area by the BET adsorption method to 0.5g/cc or more 1.0g[/cc] or less(6) wide-angle X-ray diffraction method (110) more than 3.5m2 / g 0.015 or more properties The shown massive graphite powder is used as a nucleus. After covering a carbon precursor on the front face of the nucleus, While improving many properties of a rechargeable lithium-ion battery by calcinating by the 700-2800-degree C temperature requirement under inert gas atmosphere, and making it the nonaqueous electrolyte rechargeable battery using the carbonaceous powder of the double layer structure in which the surface of a carbonaceous object was made to form, high-energy density-ization can be attained.
[0015] The above (1) The massive graphite particle which has the property of - (6) is a high grade, and

the natural or artificial shape of a scale and scale-like graphite of high crystallinity Chamfering-trituration and ****-trituration, By collecting what has the large thickness of a graphite powder, i.e., what is close to a globular form also in a scale-like particle, in process of sieving after balling-up trituration, specific surface area is not increased to ** and others, and tapping density can obtain 0.5 or more particles. Moreover, that the X diffraction peak intensity ratio of/(004) by the wide angle X-ray diffraction method (110) at this time indicates 0.015 or more to be is good. Furthermore, it is the degree of mean-circle form (the boundary length of a granular-structure product equivalent circle is used as a molecule, and the boundary length of the picturized particle projection image by the ratio made into the denominator). it is set to 1, so that a particle image is close to a perfect circle, and a particle image is long and slender -- it is -- it is -- such a small value that it is carrying out convexo-concave one -- becoming -- that which is spheroidizing as 0.940 or more and a configuration factor is good Although the method of carrying out chamfering and sifting out after grinding to the shape of a disk and a tablet-like particle is raised, if it is process in which a scale-like graphite particle is further pulverized with a fluid energy grinder as an example and is the graphite particle which shows the physical properties of above-mentioned (1) - (6), especially the creation method will not be limited.

[0016] Although used suitably [10-30 micrometers of mean particle diameters of the above-mentioned graphite powder], 12-26 micrometers is more desirable, and 15-23 micrometers is the most desirable. At this time, when content of the powder which exceeds 10% or less or the particle size of 25 micrometers for the content of powder with a particle size of less than 10 micrometers preferably 20% or less is preferably made into 10% 20% or less, it is still more desirable. Furthermore, respectively, when the content of the powder exceeding the particle size of less than 10 micrometers and the particle size of 25 micrometers reaches 10% or less preferably and considers as 10% or less preferably 20% or less, respectively, it is the most desirable 20% or less. Although the specific surface area by the BET adsorption method can use the thing of the range of 3.5-10.0m2 / g, its 4.0-8.0m2 / g are desirable, and its 4.0-7.0m2 / g are the most desirable.

[0017] The graphite particles which carried out in this way and were selected although the theoretical values of the capacity per 1g of carbon on the basis of C6 Li of the intercalation compound which the intercalation of the lithium ion is carried out and it generates were 372mAh(s) are a charge-and-discharge rate 0.2 mA/cm2 Electric capacity measurement by the half cell using the lithium metal counter electrode carried out is performed, and if the amount of specific volume is more preferably close to 350 or more mAh/g and the above-mentioned geometric capacity, it will be suitably used by 330 or more mAh/g of nearer things.

[0018] As a carbon precursor for covering the graphite particle nucleus front face which can be used by this invention, first as the organic substance which advances carbonization by the liquid phase Coal system heavy oil, such as a coal tar pitch from a soft pitch to a hard pitch, and a coal liquid, Petroleum system heavy oil, such as naphtha tar division-into-equal-parts solution system heavy oil which carries out a byproduction at the time of pyrolysis of direct-current system heavy oil, such as an asphaltene, a crude oil, naphtha, etc., Heat treatment pitches, such as an ethylene tar pitch obtained by heat-treating decomposition system heavy oil, FCC decantation oil, and the Ashland pitch, etc. can be used. Furthermore, it is vinyl system macromolecules, such as a polyvinyl chloride, a polyvinyl acetate, a polyvinyl butyral, and polyvinyl alcohol, and 3. - 3 A methyl phenol formaldehyde resin, 5 - Matter, such as sulfur ring compounds, such as nitrogen ring compounds, such as aromatic hydrocarbons, such as substitution phenol resin, such as a dimethylphenol formaldehyde resin, an acenaphthylene, a deca cyclene, and an anthracene, a phenazine, and an acridine, and a thiophene, is raised. Moreover, a thermosetting resin raw material like thermosetting resin, such as aromatic system polymer, such as chain-like vinyl resin, such as naturally-ocurring polymers, such as a cellulose, a polyvinylidene chloride, and a polyacrylonitrile, and a polyphenylene, a furfuryl alcohol resin, phenol-formaldehyde resin, and an imido resin, or furfuryl alcohol as the organic substance which advances carbonization etc. is raised with solid phase. Suitably, by choosing a solvent and carrying out dissolution dilution, these organic substance is made to adhere to the front face of a graphite particle nucleus, and can be used if needed.

[0019] Although the carbonaceous powder of the double layer structure which made the surface of a carbonaceous object form in the front face of a graphite particle nucleus finally by usually heating what mixed this graphite particle nucleus and carbon precursor in the invention in this application, obtaining an intermediate product, carbonization-calcinating and grinding after that is obtained The rate of the carbonaceous object in the carbonaceous powder of a double layer structure is adjusted so that it may become [50 or less % of the weight] 2 % of the weight or more 10 or less % of the weight preferably especially 1% of the weight or more 15 or less % of the weight still more preferably 0.5% of the weight or more 25 or less % of the weight 0.1% of the weight or more.
[0020] The manufacturing process for on the other hand obtaining the double layer carbonaceous object which the invention in this application requires is divided into the following four processes.
[0021] The 1st process graphite particle, a carbon precursor, the process that is further mixed using a mixer, a kneading machine, etc. of various marketing of a solvent if needed, and obtains mixture.
[0022] The process which obtains the intermediate product which heated stirring the aforementioned mixture if needed [2nd process], and removed the solvent.
[0023] The process which heats the 3rd process aforementioned mixture or an intermediate product at 700 degrees C or more 2800 degrees C or less under inert gas atmosphere, such as nitrogen gas, carbon dioxide gas, and argon gas, and obtains the carbonization matter.
[0024] The process which carries out [processing / classification / pulverization, a crack,] fine-particles processing of the 4th process aforementioned carbonization matter if needed.
[0025] These the in-process 2nd process and, and the 4th process can be skipped depending on the case, and the 4th process may be performed before the 3rd process.
[0026] Moreover, as heat-treatment conditions for the 3rd process, heat history temperature conditions are important. Although the temperature minimum changes a little also with the kind of carbon precursor, and its heat histories, it is usually 900 degrees C or more preferably 700 degrees C or more. On the other hand, upper limit temperature can be raised to the temperature which does not have the structure order exceeding the crystal structure of a graphite particle nucleus fundamentally. Therefore, as upper limit temperature of heat treatment, 2800 degrees C or less are usually 2000 degrees C or less and a range with 1500 degrees C or less it is still more desirable and desirable preferably. In such heat treatment conditions, a programming rate, a cooling rate, heat treatment time, etc. can be arbitrarily set up according to the purpose. Moreover, after heat-treating in a low-temperature field comparatively, a temperature up can also be carried out to predetermined temperature. In addition, one set or two or more sets are sufficient as the reaction machine used for this process also at a batch process or continuous system again.
[0027] Thus, the carbonaceous powder material of the double layer structure of the invention in this application in which the surface of a carbonaceous object was made to form It is beyond the nuclear value not to exceed the degree of crystallinity of the graphite material used as a nucleus in the peak intensity ratio R value by Raman spectrum analysis and the value of d002 and Lc which are obtained in the diffraction diagram of X-ray wide angle diffraction, i.e., an R value. d002 value of half-value-width deltav is beyond the nuclear value beyond the nuclear value, and, as for Lc, it is desirable that it is below the nuclear value. As an R value of the carbonaceous powder material of a concrete double layer structure, it is mentioned preferably 1.0 or less [0.01 or more] that it is or more 0.2 0.4 or less range still more preferably, and is [or more 0.05] beyond a nuclear value 0.6 or less [0.1 or more] more preferably 0.8 or less. Moreover, although that whose mean particle diameter is 11-40 micrometers is used suitably, 13-30 micrometers is more desirable, and 16-25 micrometers is the most desirable. At this time, when content of the powder which exceeds 10% or less or the particle size of 25 micrometers for the content of powder with a particle size of less than 10 micrometers preferably 20% or less is preferably made into 10% or less 20% or less, it is still more desirable. Furthermore, respectively, when the content of the powder exceeding the particle size of less than 10 micrometers and the particle size of 25 micrometers reaches 10% or less preferably and considers as 10% or less preferably 20% or less, respectively, it is the most desirable 20% or less. Moreover, that whose average of the thickness of the thinnest portion of a particle is below 4-micrometer or more mean particle diameter is desirable.

furthermore, the specific surface area by the BET adsorption method -- 1.0-5.0m2 / g -- more -- desirable -- 1.5-4.0m2 / g -- the thing of 2.0-3.5m2 / g is used suitably still more preferably Although the tapping density of the carbonaceous powder material of a double layer structure improves further rather than the nucleus graphite material used by carbon covering, it is desirable to control in the range of 0.7-1.2g/cc. The carbonaceous powder included in such a range is mixed with a binder or various additives, and it fabricates so that it can be used as an electrode by methods, such as an application and sticking by pressure, on charge collectors, such as copper and nickel. The density (it is called plate density below) of the active material layer on an electrode is adjusted by rolling out by the monotonous press, the roll press, etc. after it. The capacity per unit volume of a cell can be pulled out to the maximum, without reducing the cell capacity at the time of low-temperature electric discharge of a cell, and a high rate discharge by carrying out to 1.5 or less [1.3 or more] more preferably by making plate density or less into 1.6 more greatly than 1.2 at this time. Thus, the cell constituted combining the created negative electrode and the metal chalcogenide type positive electrode for lithium ion batteries usually used can realize the 4V class high voltage, and its capacity is large, the irreversible capacity accepted in an initial cycle is small, the shelf life and reliability of a cell in the neglect under an elevated temperature are high, and it excels in a high-rate-discharge property and the electric discharge property in low temperature extremely. LixMO2 (M is one or more sorts of transition metals and x= 0 to 1.2) is suitable, and the chalcogenide type positive electrode in this case is LixCoO2, LixNiO2, and LixMn 2O4 especially. And what replaced a part of those Co(es), nickel, and Mn by elements, such as other transition metals, is suitable.

[0028] Although especially this invention does not limit the electrolytic solution, it is suitable to make into a principal component a chain-like carbonate [, such as one or more sorts of annular carbonate, such as the ethylene carbonate and propylene carbonate which are excellent in oxidation resistance and a low-temperature property as a solvent of the electrolytic solution used for the cell using the above-mentioned 4 Class V positive electrode and the negative electrode of this invention, and butylene carbonate, dimethyl carbonate and diethyl carbonate, and ethyl methyl carbonate, / one or more sorts of] mixed solvent. Moreover, other solvents, such as an aliphatic carboxylate and ether, are mixable if needed. a mixing ratio -- a rate -- volume conversion -- annular carbonate -- the solvent whole -- 20 - 80% of range has desirable chain-like carbonate 10 to 90% 15 to 40% especially 5 to 50% especially

[0029] Moreover, when using [class / 3V] the material of low voltage for a positive electrode comparatively, solvents other than the above-mentioned solvent can also be used.

[0030] Lithium salt is used for the solute of these solvents. the lithium salt generally known -- LiClO4, LiBF4, LiPF6, LiAlCl4, LiSbF6, LiSCN, LiCl, LiCF3 SO3, LiCF3 CO2, Li (CF3 SO2)2, LiAsF6, and LiN (CF3 SO2)2 etc. -- it is

[0031] About selection of a required member, restrictions are not prepared at all on cell composition other than the above.

[0032] The cell using the carbonaceous powder material of the double layer structure in which the surface of the above-mentioned carbonaceous object was made to form as a negative electrode improves high charge/discharge capability ability and the high-rate-discharge performance in low temperature compared with the cell using the carbonaceous powder material of the double layer structure in which the surface of a carbonaceous object was made to form using the graphite particle which does not have the graphite particle or the property of above-mentioned (1) - (6) of not making the surface of a carbonaceous object forming as a negative electrode. Moreover, it is hard to make the organic solvent in the electrolytic solution decompose also under an elevated temperature, and since it becomes that it is hard to carry out elevation of cell internal pressure, the liquid spill accident of the electrolytic solution which was a problem conventionally can be prevented. Moreover, since specific surface area becomes small by making it the carbonaceous powder of a double layer structure, also under an elevated temperature, it is hard to make the organic solvent in the electrolytic solution decompose, and degradation of the cell performance in an elevated temperature can be made small.

[Translation done.]

* NOTICES *

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2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

EXAMPLE

[Example] Hereafter, the operation gestalt of this invention is explained in detail using a chart.
[0034] (Measuring method)
(1) About one cc of 2vol% solution of polyoxyethylene (20) sorbitan monolaurate was used for the volume criteria mean-particle-diameter surfactant, this was beforehand mixed to carbonaceous powder, and the volume criteria mean particle diameter (median size) was measured by making ion exchange water into a dispersion medium after an appropriate time with the laser diffraction formula particle-size-distribution plan "LA-700" by Horiba, Ltd.
[0035] (2) After using the screen of 300 micrometers of openings, dropping fine particles in the 20 cc tapping cell and filling up with a cell to the limit, to the screen which a sample penetrates using a tapping density Seishin Enterprise milling volume density measuring instrument "tap DIN sir KYT-3000", tapping which is 10mm of stroke length was performed 1000 times, and the tapping density at that time was measured to it.
[0036] (3) After heating at 350 degrees C as predrying and pouring nitrogen gas for 15 minutes using 8000, it measured by the one AMS[by BET specific surface area measurement Ohkurariken CO., LTD.]-BET method in the phase counter pressure 0.3 by nitrogen gas adsorption.
[0037] (4) To the X diffraction sample, about 15% of X-ray standard high-purity-silicon powder was added, it mixed, the sample cell was stuffed, the CuK alpha rays monochrome-ized with the graphite monochromator were made into the line source, and the wide angle X diffraction curve was measured by the reflective formula differential-gear RAKUTO meter method. Based on the **** method, the size (Lc) of the microcrystal of the spacing (d002) of a field (002) and C shaft orientations was measured for the wide angle X diffraction curve obtained by measurement.
[0038] (5) the Raman assay-date book -- a spectrum -- shrine make -- the Raman spectrum analysis using Ar-ion-laser light with a wavelength of 514.5nm using NR-1800 -- setting -- the intensity IA of the peak PA of a near [1580cm-1], and the intensity IB of the peak PB of the range of 1360cm-1 -- measuring -- the ratio of the intensity -- R=IB/IA was measured Moreover, the half-value width of the peak PA of a near [1580cm-1] was asked for the wave number (cm-1) as a unit. It measured by rotating a cell in a field perpendicular to a laser beam, having filled up the cell with the thing of a powder state by natural fall, and irradiating a laser beam on the sample front face in a cell in manufacture of a sample.

[0039] (6) The average of the thickness in the average carbon-powder end of the thickness of the thinnest portion in the end of a carbon powder searched for the molding object from the SEM image of the pressurization direction and the field cut to parallel, after carrying out pressing of each sample offering graphite powder using metal mold. That is, 100 or more values of the thickness direction of the thinnest portion in the end of a carbon powder were measured, and the average was calculated.
[0040] (7) Using metal mold, the X-ray peak intensity ratio of measurement (110)/(004) of the X-ray peak intensity ratio of (110)/(004) pressurized the end of a carbon powder, fabricated it with a density of about 1.7 g/cc in the shape of a pellet, computed the peak intensity ratio of/(004) obtained by wide angle X diffraction measurement (110), and calculated the average. (004) The diffraction line of a field and a

field (110) is a diffraction line in the carbon six membered ring reticulated flat surface of a graphite crystal, and its vertical plane. When there are many scale configurations, compared with the case where there are many graphite particles of the shape of the shape of a disk and a tablet, a graphite particle carries out orientation to a pressurization side and a parallel direction alternatively at the time of pellet creation. Therefore, if a scale-like particle increases compared with the graphite particle of the shape of the shape of a disk, and a tablet (110), a /(004) peak intensity ratio will become small.

[0041] (8) The flow formula particle image analysis apparatus "FPIA-1000" by measurement TOA Medical Electronics Co., Ltd. of the degree of mean-circle form was used, the graphite particle distributed in water was picturized every [1/] 30 seconds by the CCD camera, and the degree of mean-circle form to all particles was computed by carrying out real-time analysis of the particle image. Ion exchange water was used for the dispersion medium, and polyoxyethylene (20) sorbitan monolaurate was used for the surfactant. the degree of mean-circle form is the ratio which used the boundary length of a particle projected-area equivalent circle as the molecule, and made the denominator the boundary length of the picturized particle projection image, it is set to 1, so that a particle image is close to a perfect circle, and a particle image is long and slender -- it is -- it is -- it becomes such a small value that it is carrying out convexo-concave one

[0042] (Example 1 of a fundamental experiment) Drawing 1 is the cross section of the coin form cell for measuring the reversible capacitance and irreversible capacity of a negative electrode of a rechargeable lithium-ion battery. In drawing 1 , spot welding of the grid 3 which becomes the inner base of the cell case 1 made from stainless steel from the expanded metal made from stainless steel is carried out beforehand, and the mixture which makes a principal component the carbon-powder end for negative electrodes of this grid 3 and a rechargeable lithium-ion battery is fixed to one as a carbon electrode 5 by the casting-in can method. The mixture of a carbon electrode 5 mixes the end for a sample offering of a carbon powder, and an acrylic binder by the ratio of 100:5 by the weight ratio. The gasket 7 made from polypropylene is attached in the periphery of the cover 2 made from stainless steel, and the metal lithium 4 is stuck to the inside of a cover 2 by pressure. After making a carbon electrode 5 carry out **** sinking in of the nonaqueous electrolyte, distributor shaft coupling of the cover 2 with gasket 7 is carried out to the cell case 1 through the separator 6 which consists of a microporosity polyethylene film, inboard is made to curl and upper-limb opening of the cell case 1 is obturated. In addition, as nonaqueous electrolyte, the organic electrolytic solution which made the concentration of 1 mol/l dissolve a 6 fluoride [phosphoric-acid] lithium in the mixed solvent of the volume ratio 1:1 of ethylene carbonate and diethyl carbonate was used. It is current density 0.3 mA/cm2 at a 20-degree C basis, using the sample offering carbon-powder end of 14 kinds for a carbon electrode 5, producing a cell, and using a positive electrode and the metal lithium electrode 4 as a negative electrode for a carbon electrode 5. It charges and discharges by the constant current. Let the amount which deintercalated and asked for the lithium from carbon be a reversible capacitance until cell voltage is set to 1.0V, after intercalating a lithium in carbon until cell voltage is set to 0V. The value which **(ed) the reversible capacitance from quantity of electricity which intercalation took was made into irreversible capacity. In addition, the charge-and-discharge final-voltage value of these test cells is negative-electrode carbon / positive electrode LiCoO2. It is mostly equivalent to charge final-voltage 4.20V of the practical use cell of a system, and discharge-final-voltage 2.75V.

[0043] tapping density was raised by the scale-like artificial graphite, the natural graphite, and the various trituration methods which grind by the conventional method and are acquired -- as artificial, natural-graphite powder (sample No.1-15), and a comparison sample with them The spherical meso carbon micro bead which graphitized the meso carbon micro bead currently indicated by JP,7-134988,A (it MCMB(s)) Sample No.16 and petroleum-pitch-coke powder (sample No.17) are made into the end for negative electrodes of a sample offering carbon powder, and the physical-properties value of these powder, the reversible capacitance mentioned above, and irreversible capacity are collectively shown in Table 1.

[0044]

[Table 1]

試料 No.	原材料	製造元	商品名	粉末物性値										電気特性	
				d002 (Å)	Lc (Å)	ラマン R値	ラマン 半値幅 (cm⁻¹)	平均 粒径 (μm)	比表 面積 (m²/g)	最薄部 平均 厚さ (μm)	タッピング 密度 (g/cc)	平均 円形度	(110)/ (004)	可逆 容量 (mAh/g)	不可逆 容量 (mAh/g)
1	人造黒鉛	ティムカル	KS15	3.36	1000以上	0.16	21.1	7.8	14.5	1.1	0.32	0.928	0.008	351	53
2	人造黒鉛	ティムカル	KS25	3.36	1000以上	0.16	21.4	10.1	11.9	1.3	0.40	0.925	0.009	353	43
3	人造黒鉛	ティムカル	KS44	3.36	1000以上	0.15	22.2	18.8	9.3	1.8	0.41	0.919	0.010	359	36
4	人造黒鉛	ティムカル	KS75	3.36	1000以上	0.15	22.2	23.7	7.2	2.1	0.44	0.918	0.011	353	35
5	人造黒鉛	日本黒鉛	SP-10	3.35	1000以上	0.18	21.2	32.5	6.9	2.4	0.41	0.927	0.012	353	32
6	人造黒鉛	日本黒鉛	SP-20	3.36	1000以上	0.15	24.0	14.9	8.7	1.8	0.23	0.937	0.010	356	40
7	天然黒鉛	エスイーシー	SNO10	3.35	1000以上	0.19	20.9	10.4	8.7	2.0	0.46	0.919	0.008	362	39
8	天然黒鉛	エスイーシー	SNO15	3.35	1000以上	0.17	21.5	12.9	7.8	2.3	0.46	0.927	0.009	361	35
9	天然黒鉛	エスイーシー	SNO20	3.36	1000以上	0.16	21.6	18.7	6.8	2.5	0.48	0.930	0.009	358	34
10	天然黒鉛	日本黒鉛	ACP-20NB	3.36	1000以上	0.18	21.6	19.0	4.9	5.4	0.64	0.947	0.038	354	23
11	天然黒鉛	日本黒鉛	ASP-20NB	3.36	1000以上	0.17	21.1	16.7	4.9	6.3	0.66	0.943	0.039	357	20
12	人造黒鉛	日本黒鉛	SP-20NB	3.36	1000以上	0.20	20.9	15.7	6.6	3.5	0.61	0.942	0.032	360	26
13	天然黒鉛	中越黒鉛	H-0	3.36	1000以上	0.21	22.0	22.3	5.6	5.6	0.65	0.940	0.035	358	24
14	天然黒鉛	中越黒鉛	H-1	3.36	1000以上	0.18	21.8	18.4	5.8	6.5	0.79	0.941	0.038	355	24
15	天然黒鉛	中越黒鉛	H-2	3.36	1000以上	0.24	22.1	17.7	6.4	5.8	0.70	0.940	0.039	356	26
16	人造黒鉛	大阪ガス	MCMB	3.37	700	0.19	25.4	5.3	2.9	5.3	1.10	0.966	0.120	295	18
17	人造黒鉛	日本黒鉛	GMW-20NB	3.37	750	0.32	25.0	17.2	5.3	8.1	0.95	0.961	0.110	298	27

[0045] The nodular-graphite powder (sample No.16) and corks powder (sample No.17) of a comparison sample of both reversible capacitances which influence an energy density greatly the result of Table 1 to whose Lc is less than 1000A were as small as less than 300 mAh/g, although irreversible capacity was comparatively small. To these, raw material is 350 mAh/g at least, and all of the reversible capacitance of sample No.1-15 of a natural graphite and artificial-graphite powder became the value approximated to the theoretical value (372 mAh/g) of the amount of specific volume. In these, the irreversible capacity of the graphite powder of sample No.10-15 is 20 - 26 mAh/g, and it attracts attention that it is smaller than that of other graphite powders (sample No.1-9).

[0046] It is understood that a reversible capacitance higher level than using for the negative-electrode material of a rechargeable lithium-ion battery a natural graphite or an artificial graphite with high degree of crystallinity and purity whose size (Lc) of the microcrystal of C shaft orientations the spacing (d002) of the field by the wide angle X diffraction (002) is less than 3.37A as a prerequisite of this invention, and is at least 1000A or more is obtained.
[0047] (Example 2 of a fundamental experiment) In the example 1 of a fundamental experiment, using the end for negative electrodes of a carbon powder (sample No.1-17) a reversible capacitance and irreversible capacity were calculated, the cylindrical shape cell was produced and the liquid spill nature at the time of carrying out elevated-temperature neglect in the state of the high-rate-discharge property in low temperature and charge was measured.
[0048] Drawing 2 is the cross section of the cylindrical shape cell of spiral electrode group composition. In drawing 2 , the band-like positive electrode 10 of one sheet each and a negative electrode 11 are spirally wound through the separator 12 which consists of a microporosity polyethylene film, and an electrode group is constituted. A positive electrode 10 is LiCoO2 which is the multiple oxide of the lithium of active material material, and cobalt. The after [dryness] roll press of the paste mixed at a rate of 100:3:10 is applied and carried out to both sides of the aluminum foil which is a charge collector by the weight ratio, and the carbon black of electric conduction material and the polytetrafluoroethylene (PTFE) of a binder are judged in a predetermined size. In addition, PTFE of a binder used the thing of a dispersion solution. Spot welding of the piece 13 of a positive-electrode lead is carried out to the aluminum foil of a positive electrode 10. A negative electrode 11 applies and carries out the after [dryness] roll press of the paste which added the acrylic binder solution in the end of a sample offering carbon powder, and was mixed to both sides of the copper foil which is a charge collector, and cuts it out in a predetermined size. Spot welding of the piece 14 of a negative-electrode lead is carried out to the copper foil of a negative electrode 11. After equipping the inferior surface of tongue of the wound electrode group with the pars-basilaris-ossis-occipitalis electric insulating plate 15 and holding in the cell case 16 made from nickel ******, spot welding of the piece 14 of a negative-electrode lead is carried out to the inner base of the cell case 16. After laying the up electric insulating plate 17 on an electrode group after that, grooving is carried out to the predetermined position of opening of the cell case 16, and it carries out pouring sinking in of the organic electrolytic solution of the specified quantity. The organic electrolytic solution same as the organic electrolytic solution as the example 1 of a fundamental experiment was used. Then, spot welding of the piece 13 of a positive-electrode lead is carried out to the inner base of the obturation board 19 with which the gasket 18 was attached in the periphery. The obturation board 19 is inserted in opening of the cell case 16 through a gasket 18, and a cell will be completed if the upper limb of the cell case 16 is curled and obturated to inboard.
[0049] The service capacity of each cell was regulated by negative-electrode capacity, and made the same carbon-powder Shigekazu Sue of each cell for negative electrodes irrespective of the kind. The amount of other part material used and the production method are completely made the same, and could be made to perform comparison in the end for negative electrodes of a carbon powder.
[0050] About cell A-Q five cells each using the carbon-powder end for negative electrodes of 17 kinds, after charging all the cells at 20 degrees C until the terminal voltage of each cell became 4.2V at 100mA (1/5C) constant current, it discharged to 2.75V by 100mA (1/5C) constant current, and 1 / 5C service capacity was calculated. Then, after charging similarly, it discharged to 2.75V by 500mA (1C) constant current, and 1C service capacity was calculated. Subsequently, after charging at 20 degrees C, it was left at -20 degrees C for 24 hours, and 1C service capacity was calculated at the same -20 degrees C. After putting each cell on 20 degrees C gently, restoring the temperature of a cell to 20 degrees C, and charging by the same cell, and it left it at 100 degrees C on the 1st and the temperature of a cell became 20 degrees C, the existence of a liquid spill was observed about all cells.
[0051] As contrasted with the physical-properties value in the end of a sample offering carbon powder, the cell performance (average of five cells) mentioned above is summarized, and it is shown in Table 2.
[0052]
[Table 2]

試料 No.	原材料	製造元	商品名	セル記号	電池性能			
					1/5C 放電容量	1C 放電容量	-20℃1C 放電容量	高温放置後 漏液数
1	人造黒鉛	ティムカル	KS15	A	511	501	450	5/5
2	人造黒鉛	ティムカル	KS25	B	532	523	452	3/5
3	人造黒鉛	ティムカル	KS44	C	539	521	410	2/5
4	人造黒鉛	ティムカル	KS75	D	549	508	357	0/5
5	人造黒鉛	日本黒鉛	SP-10	E	537	483	267	1/5
6	人造黒鉛	日本黒鉛	SP-20	F	541	528	433	2/5
7	天然黒鉛	エスイーシー	SNO10	G	538	522	473	3/5
8	天然黒鉛	エスイーシー	SNO15	H	545	531	452	2/5
9	天然黒鉛	エスイーシー	SNO20	I	536	520	407	1/5
10	天然黒鉛	日本黒鉛	ACP-20NB	J	554	543	421	0/5
11	天然黒鉛	日本黒鉛	ASP-20NB	K	561	550	445	0/5
12	人造黒鉛	日本黒鉛	SP-20NB	L	557	546	440	0/5
13	天然黒鉛	中越黒鉛	H-0	M	553	541	420	0/5
14	天然黒鉛	中越黒鉛	H-1	N	554	545	440	0/5
15	天然黒鉛	中越黒鉛	H-2	O	560	548	445	0/5
16	人造黒鉛	大阪ガス	MCMB	P	478	463	417	0/5
17	人造黒鉛	日本黒鉛	GMW-20NB	Q	483	468	372	0/5

[0053] sample No. whose reversible capacitance shown from Table 2 in Table 1 was small -- although 20-degree C 1/5C and 1C service capacity of 16 and 17 are low, they of the graphite powder of sample No.1-15 are relatively large That however, the high-rate-discharge capacity (-20 degrees C, 1C) in low temperature showed 400mA or more among sample No.1-15 They were sample No.1 and the cells A, B, C, F, G, H, I, J, K, L, M, N, and O by the graphite powder of 2, 3, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15. Furthermore, it was the cells D, J, K, L, M, N, O, P, and Q by sample No.4 and the carbon-powder end of 10, 11, 12, 13, 14, 15, 16, and 17 that a liquid spill was not accepted at all after elevated-temperature neglect. Ranging from these results to all cell performances, sample No.10 and the cells J, K, L, M, N,

and O by the graphite powder of 11, 12, 13, 14, and 15 were excellent.
[0054] (An example and example of comparison) In the cell which measured the liquid spill nature at the time of leaving it in the example 2 of a fundamental experiment under 1 / 5C service capacity, 1C service capacity, -20-degree C 1C service capacity, and an elevated temperature The cell J by the graphite powder of sample No.10, and 11, 12, 13, 14 and 15 which was excellent covering all cell properties After leaving the cell of K, L, M, N, and O under an elevated temperature, when 20-degree C 1 / 5C service capacity were calculated on the charge-and-discharge conditions indicated for the example 2 of a fundamental experiment, compared with 1 / 5C service capacity before leaving it under an elevated temperature, only 70 - 80% of service capacity was shown. Although the reliability of a cell improved, degradation of a cell property is intense, and when left under an elevated temperature, it is necessary for the liquid spill accident by the neglect under an elevated temperature to have none of these cells, and to make degradation of a cell property small.
[0055] Then, by using as a nucleus the end for negative electrodes of a carbon powder (sample No.1-17) the cell performance was measured in the example 2 of a fundamental experiment, finally it heat-treated at 1200 degrees C under the inert gas style after covering, respectively, so that it might become 5% of the weight after carbonization, using the petroleum system tar pitch obtained at the time of naphtha cracking as a carbon precursor. Then, it cracked after cooling using the grinder to the room temperature, and the end of a carbon system composite powder with the fixed particle size distribution was obtained. In this way, the carbonaceous powder (sample No.18-34) of the double layer structure which made the surface of a new carbonaceous object form on a nuclear front face was created, and it considered as the end for negative electrodes of a sample offering carbon powder.
[0056] having produced each five cell of cell R-AH like the example 2 of a fundamental experiment, respectively, and having measured the same cell performance except having used the carbon-powder end for negative electrodes of 17 kinds, -- in addition, 1 / 5C service capacity of a cell as which the liquid spill after elevated-temperature neglect was not regarded were measured
[0057] The cell performance mentioned above to the physical-properties value in the end of a sample offering carbon powder is collectively shown in Table 3.
[0058]
[Table 3]

試料 No.	核材試料 No.	原材料	製造元	商品名	粉末物性値 平均粒径 (μm)	比表面積 (m²/g)	最薄部平均厚さ (μm)	タッピング密度 (g/cc)	セル記号	電池性能 1/5C放電容量 (mAh)	1C放電容量 (mAh)	-20℃ 1C放電容量 (mAh)	高温放置後漏液数	高温放置後1/5C放電容量 (mAh)	高温放置前後の1/5C放電容量比 (%)
18	1	人造黒鉛	ティムカル	KS15	12.0	4.9	1.9	0.47	R	520	513	448	4/5	-	-
19	2	人造黒鉛	ティムカル	KS25	12.4	4.5	2.4	0.57	S	542	530	454	2/5	-	-
20	3	人造黒鉛	ティムカル	KS44	17.7	4.2	2.6	0.61	T	549	532	411	1/5	-	-
21	4	人造黒鉛	ティムカル	KS75	23.2	3.1	3.1	0.74	U	553	520	357	0/5	455	82.3
22	5	人造黒鉛	日本黒鉛	SP-10	38.8	2.5	3.3	0.62	V	547	490	269	1/5	-	-
23	6	人造黒鉛	日本黒鉛	SP-20	22.9	4.8	2.7	0.57	W	549	535	434	2/5	-	-
24	7	天然黒鉛	エスイーシー	SNO10	18.6	4.1	3.1	0.82	X	541	530	475	2/5	-	-
25	8	天然黒鉛	エスイーシー	SNO15	21.4	3.7	3.2	0.81	Y	554	537	452	1/5	-	-
26	9	天然黒鉛	エスイーシー	SNO20	25.2	2.9	3.4	0.83	Z	542	528	409	1/5	-	-
27	10	天然黒鉛	日本黒鉛	ACP-20NB	20.2	2.6	8.1	0.81	AA	566	552	423	0/5	531	93.8
28	11	天然黒鉛	日本黒鉛	ASP-20NB	21.4	2.8	10.2	0.88	AB	569	559	447	0/5	534	93.8
29	12	人造黒鉛	日本黒鉛	SP-20NB	21.5	2.8	4.9	0.70	AC	567	549	443	0/5	532	93.8
30	13	天然黒鉛	中越黒鉛	H-0	24.8	2.3	7.6	0.85	AD	560	550	425	0/5	530	94.6
31	14	天然黒鉛	中越黒鉛	H-1	24.0	2.4	10.5	0.94	AE	561	552	458	0/5	532	94.8
32	15	天然黒鉛	中越黒鉛	H-2	21.2	2.6	8.3	0.92	AF	563	557	462	0/5	537	95.4
33	16	人造黒鉛	大阪ガス	MCMB	6.5	1.8	6.1	1.26	AG	485	570	415	0/5	450	92.8
34	17	人造黒鉛	日本黒鉛	GMW-20NB	17.2	1.6	8.7	1.05	AH	487	473	374	0/5	452	92.8

[0059] From Table 3, change of 1 / 5C service capacity by making it the carbonaceous powder of a double layer structure, 1C service capacity, and -20-degree-C1C service capacity was not seen. However, the cell R by the carbonaceous powder sample (No.18, 19, 20, 22, 23, 24, 25, 26) of sample No.1 as which the liquid spill was regarded in the example 2 of a fundamental experiment, and the double layer structure which used 2, 3, 5, 6, 7, 8, and 9 as the nucleus Although the number of liquid spills of S, T, V, W, X, Y, and Z showed the inclination which decreases, it was inadequate for stopping a liquid spill. On the other hand, it was the cells U, AA, AB, AC, AD, AE, AF, AG, and AH by the carbonaceous powder of the double layer structure of samples 21, 27, 28, 29, 30, 31, 32, 33, and 34 that

a liquid spill was not accepted at all after elevated-temperature neglect. 1 / 5C service capacity after elevated-temperature neglect of these cells became 82 - 96% of value to 1 / 5C service capacity before elevated-temperature neglect, and 1 / 5C service capacity after elevated-temperature neglect improved by making it the carbonaceous powder of a double layer structure. In these, all 1 / 5C service capacity after elevated-temperature neglect are at least 530 or more mAhs, and the cells AA, AB, AC, AD, AE, and AF by the carbonaceous powder of the double layer structure of samples 27, 28, 29, 30, 31, and 32 became 93% or more of value to 1 / 5C service capacity before elevated-temperature neglect. Ranging from these results to all cell performances, the cells AA, AB, AC, AD, AE, and AF by the carbonaceous powder of sample No.27 and the double layer structure of 28, 29, 30, 31, and 32 were excellent.

[0060] In addition, although burning temperature was carried out at 1300 degrees C in order to obtain the carbonaceous powder of a double layer structure in the above, by the 700 degrees C - 2800 degrees C temperature requirement, the same powder physical properties were acquired and the same effect as this invention was seen. Moreover, although the carbonaceous powder of a double layer structure mixed and produced the charge of karyomitome, and the pitch so that the weight ratio of the graphite powder used for the nucleus and the carbon matter in which the surface was made to newly form might be set to 95:5, physical properties with these weight ratios same in 99:1-50:50 were acquired, and the same effect as this invention was acquired.

[0061] Moreover, in the above, although only the organic electrolytic solution was explained as nonaqueous electrolyte about this invention, it does not bar applying to the rechargeable battery which consists of cation conductivity solid electrolytes, such as polymer.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] Book
[Drawing 2] The cross section of the cylindrical shape cell of the spiral electrode group composition by the operation gestalt of this invention.
[Description of Notations]
1: Cell case
2: Cover
3: Grid
4: Metal lithium electrode
5: Carbon electrode
6: Separator
7: Gasket
10: Positive electrode
11: Negative electrode
12: Separator
13: The piece of a positive-electrode lead
14: The piece of a negative-electrode lead
15: Pars-basilaris-ossis-occipitalis electric insulating plate
16: Cell case
17: Up electric insulating plate
18: Gasket
19: Obturation board

[Translation done.]

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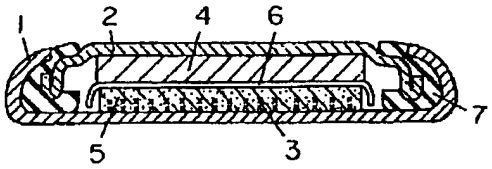
DRAWINGS

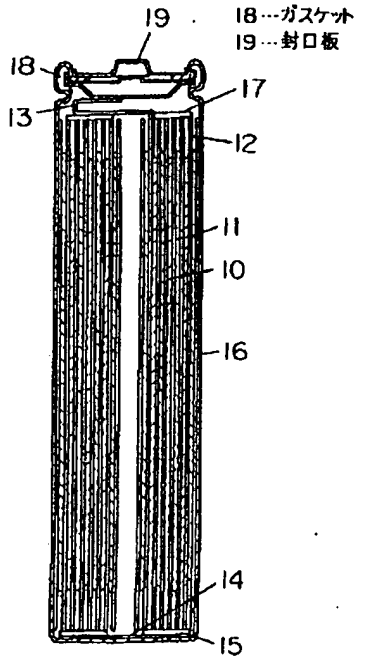
[Drawing 1]

1…セルケース
2…ふた
3…グリッド
4…金属リチウム電極
5…炭素電極
6…セパレータ
7…ガスケット



[Drawing 2]

10…正極
11…負極
12…セパレータ
13…正極リード片
14…負極リード片
15…底部絶縁板
16…セルケース
17…上部絶縁板
18…ガスケット
19…封口板



[Translation done.]